CHEMICAL AND BIOLOGICAL FACTORS AFFECTING THE PERFORMANCE OF CCA AND ACA TREATED WOOD IN SOIL

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ABSTRACT

The performance of CCA and ACA treated wood in soil contact has been investigated with particular reference to the effect of high concentrations of nitrogen on the decay process, fixation and leachability of preservative elements and the role of lignin in the binding of nitrogen and preservative elements to wood.

Concentrations of surface nutrients, including nitrogen, present in CCA treated small blocks of both the hardwood lime (*Tilia vulgaris*, Hayne) and the softwood pine (*Pinus sylvestris*, L) exposed to soil, increased the toxic thresholds of CCA and accelerated nitrogen transfer to the wood. Wood blocks treated with low concentrations of CCA showed significant losses of preservative elements and the presence of surface nutrients increased the percentage losses observed.

The effect of air-drying, after two weeks of curing at high relative humidity, in minimising the leachability of CCA from treated wood blocks of lime and pine was investigated. Percentage losses of both copper and chromium, during aqueous leaching, were very similar from undried and air-dried blocks.

The leachability of preservative elements from CCA treated lime and pine blocks leached in distilled water, aqueous soil extract or a bacterial suspension in an aqueous soil extract were compared. Neither soluble components of soil, nor large numbers of soil bacteria caused significant solubilisation of CCA.

ACA treated lime, pine and spruce (*Picea sitchensis*, Carr) blocks contained elevated levels of nitrogen and ammonium nitrogen, relative to untreated blocks, both before and after aqueous leaching and nitrogen contents of blocks increased with increasing ACA treating concentration. During aqueous leaching, approximately 20% of the copper was lost from blocks at all ACA treating concentrations.

Toxic thresholds of the fungicide copper in ACA treated lime, pine and spruce blocks were determined in a large-scale soil burial experiment. The toxic thresholds for ACA treated lime and pine blocks were higher than those for

similar blocks treated with CCA, previously exposed to soil. Considerable nitrogen inputs from soil to ACA treated wood blocks occurred during the decay process. Losses of copper from unleached ACA treated blocks exposed to soil exceeded those observed during aqueous leaching.

The lignin nitrogen contents of untreated and ACA treated pine blocks increased during soil burial. This accumulation of nitrogen on lignin was associated with an increase in wood nitrogen content and with decay.

Aqueous leaching of CCA treated normal, holocellulose and periodate lignin blocks of lime and pine showed that the majority of each preservative element was resistant to leaching from both the lignin and polysaccharide fractions of wood. Percentage losses of preservative elements were higher from holocellulose than from lignin.

The implications of the findings of these studies in relation to the performance of CCA and ACA treated timber in service in soil contact are discussed.

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CHAPTER 1

INTRODUCTION

Introduction

In common with most forms of dead plant material, wood is subject to rapid decomposition in soil. Soil is the primary source of many micro-organisms capable of decaying wood and therefore contact of wood with soil leads to the rapid onset of decay. The moisture retaining properties of soil also maintain the wood moisture content at a level conducive to decay, even during dry weather conditions. Such factors as the level of microbial activity, nutrient availability, acidity and aeration in soil determine the rate of decay of wood emplaced in it. Therefore, soil type influences the decay rate considerably, decay generally being more rapid in light porous soils with a high humus content than in heavy, poorly drained clay soils (Cartwright and Findlay, 1958).

Timber employed in soil contact for such purposes as fence posts and transmission poles decays rapidly unless a suitable wood preservative is employed. A number of preservative formulations are available for use in timber in soil contact. One of the most widely used for this purpose is the water borne copper chrome arsenic CCA solution (BS4072, 1974). It has been shown that wood apparently well treated with CCA is also often subject to decay. This decay problem has been highlighted (Aston and Watson, 1976) by the

failure on a worldwide scale of CCA treated woods, generally hardwoods, in soil contact.

This problem is of considerable economic significance since preservative treated timber is not a cheap commodity. In Britain, for example, the cost of replacement of a single preservative treated transmission pole is over £200 and there are approximately six million Electricity Board transmission poles nationwide.

In tropical regions, decomposition of timber is caused by both fungi and insects, but in temperate regions decomposition is due mainly to micro-organisms (Findlay, 1985). Forest ecosystems produce vast amounts of litter annually, much of it in the form of woody materials. This has led to the evolution of fauna and microflora specifically adapted to decay wood.

Wood is a heterogenous substance and its anatomical structure and chemical composition are of great importance in determining both its susceptibility to decay and its treatability with wood preservatives.

The considerable differences between hardwoods and softwoods in both anatomy and chemical constituents result in differences in the decay susceptibility of the two wood types both in the presence and absence of wood preservatives.

The anatomy of wood

Softwoods

Over 90% of the total wood volume of softwoods is made up of tracheids, vertically oriented hollow cells, square to rectangular in cross-section with closed tapered ends that overlap. They are about 3.5 mm long and 35 µm wide (Gray and Parham, 1982). They provide both a vertical passage for sap and strength to the living tree. Adjoining tracheids are linked by means of pits. A pit membrane exists between the pairs of pits in adjacent tracheids. The thickened centre of the membrane, known as the torus, is attached to the periphery by fibrous strands of the margo region. Ray cells, running radially through the tree stem, distribute and store food in the living tree. Where they come into contact with tracheids, "cross-field" pits exist to facilitate movement of food materials from ray cells to developing tracheids. Four important commercial genera of softwoods, *Pinus*, *Picea*, *Pseudotsuga* and *Larix* also possess resin ducts running in both the vertical and horizontal planes (Jane, 1970).

Hardwoods

The main structural cells in hardwoods are wood fibres which comprise over 80% of the total wood volume. They are much shorter than softwood tracheids averaging

about 2 mm in length (Jane, *op cit*) with smaller lumens, thicker walls and fewer pits. In the majority of hardwoods, the vertical movement of sap occurs mostly in vessels which are short (0.02 - 0.5 mm), thin-walled and joined end to end. Their diameter varies considerably according to wood species. Thin-walled longitudinal parenchyma cells distributed in the vertical plane act as food storage cells. Hardwoods also possess ray cells similar to those of softwoods and liquid translocation between these cells and vessels and fibres occurs through pits. However the hardwood pit membranes lack the torus found in softwood pits.

During the impregnation of timber with liquid preservatives, penetration is mostly in a longitudinal direction since there are fewer cell walls to obstruct the movement of liquid up the tree stem than there are in the radial direction. The rate of diffusion of water in a longitudinal direction may be up 10^3 to 10^5 times as fast as in a radial direction (Jane, *op cit*). In hardwoods, longitudinal movement of preservatives through wood occurs mostly in the vessels whilst radial diffusion into the surrounding fibres may be slow. In softwoods, longitudinal movement of preservatives is directly through the tracheids and the pits linking them. Radial penetration of preservatives in both hardwoods and softwoods is assisted by the ray cells.

In some softwoods, notably of the genera *Picea* and *Pseudotsuga*, the drying of green sapwood or the conversion of sapwood to heartwood leads to the torus at the centre of pit membranes being drawn to one side and becoming tightly bound to the tracheid wall, forming an "aspirated pit". This process greatly reduces the permeability of the wood to fluids. Such refractory wood types are difficult to treat with preservatives by standard impregnation procedures.

Refractory wood species may be more effectively treated with wood preservatives by treating the timber in an unseasoned green form using a sap displacement process, since in green wood aspirated pits have not formed. However, even this approach does not always lead to the adequate penetration of the sapwood of the refractory spruces with water borne preservatives (Evans, Smith and King, 1986).

Chemical constituents of wood

Wood is highly hygroscopic and in moist conditions such as in soil can contain more than its own dry weight of water.

Dry wood is comprised mainly of three polymeric materials: cellulose, hemicellulose and lignin. These collectively make up more than 95% of the total wood substance, the remainder being small amounts of nitrogenous

materials, pectin, starch, low molecular weight sugars and minerals. Pectin, starch and sugars may be of considerable importance as carbon sources for the early microbial colonisers of wood (Hulme and Shields, 1970).

Cellulose makes up between 40 and 50% of the total weight of most wood types (Kirk, 1973). It is a linear polymer of anhydro-D-glucopyranose units linked by glycosidic bonds. Each molecule of cellulose contains between about 7,000 and 10,000 glucose residues. In wood cell walls, the individual cellulose molecules are organised into linear bundles forming elementary fibrils bound laterally by hydrogen bonds. It is thought that the individual fibrils may be aggregated together into ribbons termed microfibrils.

Hemicelluloses are also polymers of anhydro-sugar units linked by glycosidic bonds. However hemicelluloses may contain several different types of sugar units, generally D-glucose, D-galactose, D-mannose, L-arabinose, D-xylose and 4-O-methyl-D-glucuronic acid. Hemicelluloses tend to be branched rather than linear and are of much lower molecular weight than cellulose. They make up approximately 20 to 34% and 12 to 18% of the dry wood substance of hardwoods and softwoods respectively.

The hemicellulose component of wood is considered to exist in an amorphous state in the cell walls, forming an interpenetrating polymer complex with lignin and surrounding the cellulose fibrils as a matrix (Kirk, *op cit*).

Lignin constitutes about 17 to 24% of hardwoods and 25 to 34% of softwoods by weight. It is a highly branched, three-dimensional polymer of oxyphenylpropane derived from three substituted cinnamyl alcohols: p-coumaryl, coniferyl and sinapyl alcohols, also known as P-hydroxyphenyl, guaiacyl and syringyl units respectively. The proportions of these alcohols differ greatly between and within hardwoods and softwoods: in softwoods, lignin is generally made up almost entirely of coniferyl alcohol whereas in hardwoods it comprises both coniferyl and sinapyl alcohols. The individual units may be linked either by the propyl side chains or by direct linkage of the phenyl rings.

The major chemical components of wood differ greatly in their susceptibility to microbial decay. Whereas cellulose and hemicellulose are easily degraded by many micro-organisms, the complex aromatic structure and chemical composition of lignin make it highly resistant to decay, except by species of Basidiomycete fungi causing white rot in wood. The presence of lignin in wood may therefore act as a barrier to the decomposition of cellulose and hemicellulose. Butcher and Nilsson (1982) found a strong

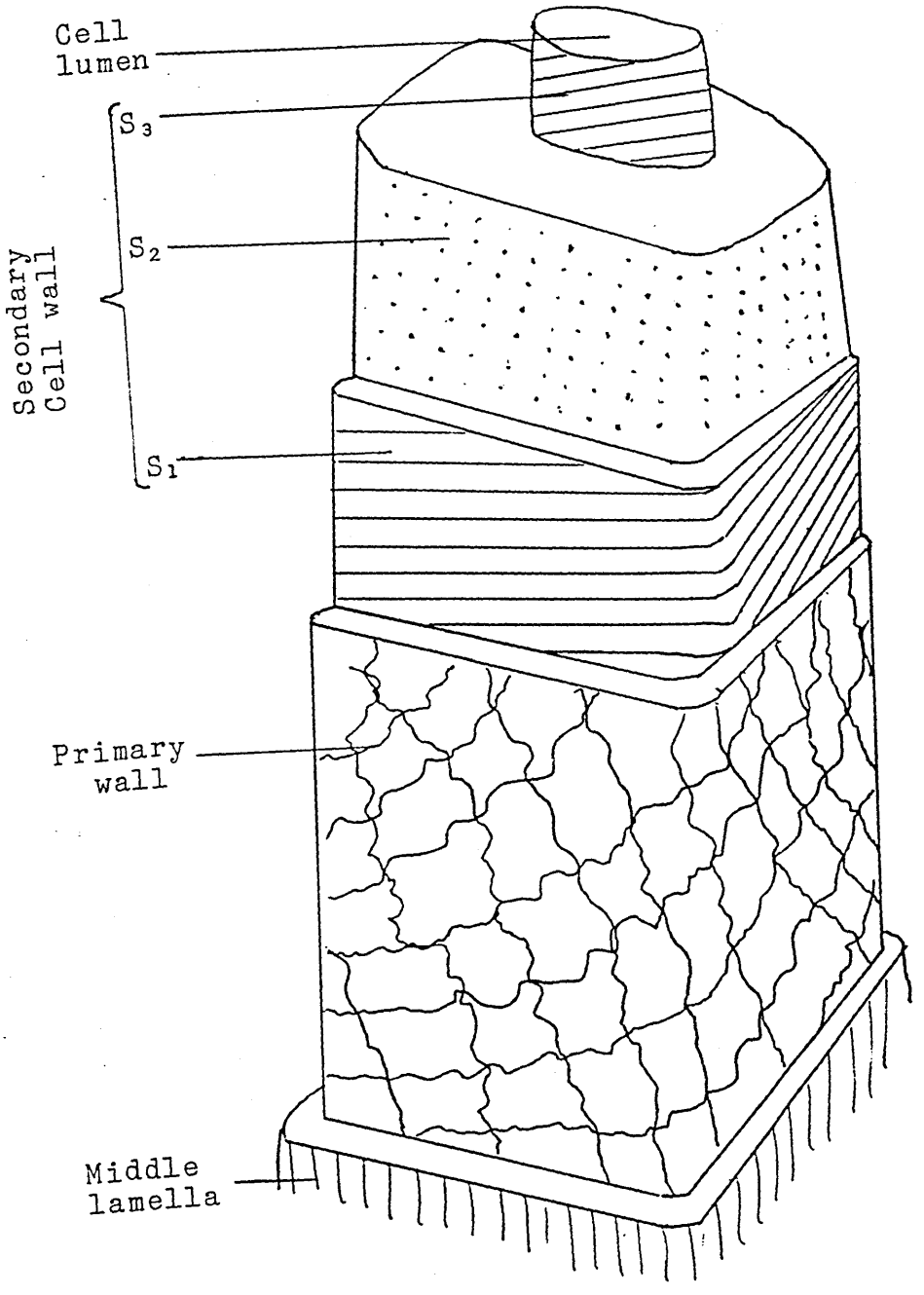
correlation between the decay susceptibilities of different wood species and their lignin content: wood with a high lignin content is generally less susceptible to microbial decay than wood with a low lignin content. The major wood components also interact differently with wood preservatives. The chemical structure of lignin includes many aromatic -OH and -COOH functional groups. Such groups are important as cation exchange sites involved in the fixation of preservative elements such as copper (II) and chromium (III) to wood. Cellulose and hemicellulose contain very few -COOH groups and only non-aromatic -OH groups. Therefore, their role in cation exchange fixation should be less than that of lignin.

Structure of wood cells and distribution of structural components

The main structural components of hardwoods and softwoods are fibres and tracheids respectively. Although the cell wall is thicker and the lumen smaller in fibres than in tracheids, both are multilayered structures of similar chemical composition.

Figure 1.1 shows a diagram of a typical wood cell. The thin middle lamella region between the individual wood cells is composed mostly of lignin. The primary wall consists of randomly oriented interwoven cellulose

Fig 1.1 Diagram of a typical wood cell



microfibrils embedded in a matrix of hemicelluslose, pectin and lignin. The secondary wall is comprised of three layers which are differentiated from one another by the orientation of the cellulose microfibrils they contain. The S_1 layer, is about 0.1 to 0.2 um thick with a microfibril orientation of 50 to 70% from the vertical axis. The S_2 layer, which comprises 70 to 75% of the total cell wall volume, is about 2 to 5 um thick with a microfibril orientation of 5 to 20^{o} from the vertical axis. The S_3 layer, adjacent to the cell lumen, is similar to the S_1 layer in thickness and has a microfibril orientation of 60 to 90^{o} from the fibre axis. Both the S_3 and S_1 layers have a higher lignin content than the S_2 layer.

Sapwood and Heartwood

The woody tissue which comprises the bulk of a tree stem is composed predominantly of dead cells. However, the ray and axial parenchyma cells, which are involved in the storage of reserve materials such as starch and fats, may remain viable for many years (Hillis, 1977). The outer part of the tree stem, which contains such viable cells, is known as the sapwood region and is responsible for the conduction of water, minerals and foods in the living tree.

In most trees, the inner portion of the stem does not conduct water and contains no viable cells. This region

of the stem is known as heartwood. Heartwood is formed when water conduction ceases in the innermost portion of the sapwood. The remaining viable parenchyma cells in this inner sapwood consequently die, their protoplasts disintegrate, cell sap and reserve materials are removed and the parenchyma cell walls may become more heavily lignified (Fahn, 1982). The removal of reserve materials may be accompanied by the development of oils, gums, tannins, resins, coloured substances and aromatic compounds which accumulate in the wood cell lumina and pit cavities (Jane, op cit) and hence heartwood is often much darker than the surrounding sapwood. During heartwood formation, bordered pits, present in the tracheids of softwoods may become aspirated, whilst in some hardwoods, parenchyma cells may form protuberances which penetrate, via pits, into adjacent vessels. These outgrowths from the parenchyma cells, known as tyloses, may completely block the vessels.

The physical and chemical changes which occur during heartwood formation render the heartwood region much less penetrable by wood preservative solutions than the surrounding sapwood. However, sapwood, which contains both soluble and insoluble food materials and lacks the resins and aromatic compounds present in heartwood, is generally far more susceptible to microbial decay than the heartwood core.

Therefore, it is the sapwood region which requires preservative protection to prevent microbial attack and

since the failure of both preservative treated and untreated timber in soil contact is due primarily to the microbial decay of sapwood, only sapwood was employed in the experiments described in this thesis.

Classes of micro-organisms decaying wood

Wood decaying micro-organisms can be classified into four major groups:

Basidiomycete fungi;

soft-rot micro-organisms (Ascomycetes, fungi imperfecti and possibly Actinomycetes and bacteria);

mould and stain fungi;

bacteria.

The Basidiomycete fungi include many species specifically adapted to decay wood. Their moisture requirements vary considerably but the dry rot fungus **Serpula lacrymans** can degrade wood with a moisture content as low as 20% (Cartwright and Findlay, op cit).

The white-rot fungi produce both ligninases and cellulases and can completely destroy wood in a comparatively short period whilst brown-rot fungi produce only cellulases and therefore cannot degrade the lignin component of wood.

The ability of Ascomycetes and fungi imperfecti to degrade wood was first recognised by Savory (1954) in cooling tower timber. These fungi can only degrade wood under high moisture conditions such as in cooling towers and soil where they are the main agents of decay of preserved timber. They cause rapid degradation of cellulose and may also cause a slow depletion of lignin (Levi and Preston, 1965). Actinomycetes (Baecker, 1982) and some bacteria (Greaves, 1968) have also been implicated in soft-rot decay.

Mould and stain fungi generally only colonise green wood, utilising readily available soluble carbohydrates and nitrogenous compounds. Although these fungi do not degrade wood, some may act as soft rot fungi (King and Oxley, 1976).

The role of bacteria in wood decay is becoming clearer (Greaves, 1971; Singh and Butcher, 1985). They are capable of utilising soluble components of wood and since some species are motile, they are likely to be early colonisers of wood submerged in water or in soil contact. In water-logged wood, bacteria may produce erosion troughs in the cell walls but such decay does

not seriously affect the wood structure. However, recent studies have identified two types of bacterial decay which may be of considerable economic importance: tunneling bacteria (Nilsson and Daniel, 1983) and cavitation bacteria (Nilsson and Singh, 1984). These bacteria may be of importance in the decay of preservative treated wood in soil contact.

Decay patterns produced by micro-organisms in wood

The structure of individual wood cells has a considerable influence on the pattern of decay produced by each group of micro-organisms. The chemical composition of the various cell layers determines their susceptibility to microbial breakdown.

Micro-organisms generally enter wood cells through pits in the primary wall/middle lamella complex linking individual vertical cells and then grow in the cell lumen. White-rot fungi can break down the whole cell wall but since the S_3 layer of the secondary cell wall is rich in lignin, it provides some protection against soft-rot and brown-rot fungi which utilise mostly the cellulose-rich S_2 layer. Kirk (*op cit*) has noted that many fungi and bacteria including *Myrothecium verucaria* and *Trichoderma viride*, which are virulently cellulolytic, are unable to degrade cellulose in wood. However, if lignin is even partially removed by chemical or biological

means, the polysaccharides become more susceptible to enzyme attack. Zainal (1976) also found very rapid degradation of cellulose in the cell wall of deligninified pine by the soft-rot fungus *Phialophora fastigiata* whilst the same fungus caused only staining of untreated pine.

Brown-rot fungi overcome the S_3 layer by producing a diffusable cellulase which can move through the S_3 layer and break down the cellulose-rich S_2 layer. The soft-rot fungi actively penetrate the S_3 layer and grow into the S_2 layer producing soft-rot cavities (Savory, *op cit*). It is thought that they penetrate the S_3 layer by enzymic action and hydrostatic forces but Nilsson (1982) has postulated the presence of "initiation sites" in the S_3 layer with a lower lignin content where soft-rot fungal hyphae can penetrate this layer and subsequently form "L" or "T"-branch soft-rot cavities in the S_2 layer.

Tunneling bacteria penetrate the S_3 layer by lytic action (Nilsson and Daniel, *op cit*) and then tunnel through the S_2 layer with each cell division giving rise to two separate tunnels formed by the daughter cells. These bacteria may also form tunnels in the S_1 layer and frequently penetrate the middle lamella to adjacent wood cells, thus suggesting that they may produce ligninases.

Cavitation bacteria produce minute holes in the S_3 layer and then form diamond shaped cavities in the S_2 layer at approximately 90^{o} to the longitudinal axis of the wood cell. Although these bacteria may produce a diffusable cellulase, which breaks down cellulose for a considerable distance around the bacterial cells, they apparently have little effect on lignin and the S_1 and S_3 layers remain intact.

Microbial succession in wood in soil

In timber free from contact with soil or water, decay tends to be caused by a few different species of basidiomycete fungi which have infected the wood. However, wood in soil contact is open to colonisation by a large number of different species of decay causing micro-organisms. Thus the microflora of timber decaying in soil can be very diverse and even if basidiomycetes are inhibited by the presence of preservatives, there are still many species of micro-organisms such as soft-rot microfungi and bacteria which can decay the wood.

Clubbe and Levy (1982) studied the microflora involved in the decay of both CCA treated and untreated pine and birch sapwood in soil. These studies involved a combination of culturing techniques and microscopic examination of the wood and showed a succession of micro-organisms in wood both before and during decay. In

untreated birch and pine, bacteria were the first colonisers but their numbers fell during the first year of exposure of the wood to soil. Primary moulds, soft-rot fungi and basidiomycete fungi became dominant with secondary moulds becoming more prominent at high levels of decay. Although birch decayed more rapidly than pine, basidiomycetes were the climax microflora in both wood types. In CCA treated wood, the pattern of succession was similar except that the basidiomycetes were inhibited and consequently soft-rot fungi were the climax microflora.

Wood Preservatives

Wood preservatives fall into three categories: preservative oils, water-borne preservatives and preservatives dissolved in oils or non-aqueous solvents.

Creosote is the main preservative oil and is produced by the distillation of coal tar. It has been used successfully for many years for any external woodwork which requires no painting. It is, however, unpleasant to handle and no longer so effective, apparently due to the removal of more volatile components during the current production processes.

Water-borne preservatives fall into four main types: mixtures of fluorides, dinitrophenates and chromates;

mixtures of copper salts with or without arsenic and chromate; zinc chloride and chromated zinc chloride; and ammoniacal solutions of copper, zinc, arsenic and borate. More recently, quaternary ammonium compounds have been extensively tested for effectiveness in timber against basidiomycete attack (Butcher, Preston and Drysdale, 1977; Butcher and Drysdale, 1977) and in soil contact (Butcher, Preston and Drysdale, 1979). The principal advantages of water-borne preservatives are: they can be transported cheaply in solid or concentrated form; the wood is clean, odourless and easily handled and can subsequently be painted over; and fire retardant salts can be added with the preservative. The chief disadvantages are: many formulations leach out of the wood in external uses; the wood must be redried after treatment; the dimensions of the timber change during treatment.

Toxins used in conjunction with oils and non-aqueous solvents include pentachlorophenol, organo-tin compounds (especially tri-butyl tin oxide), monochloronaphthalene and naphthenates of copper and zinc. The solvent used is normally a volatile oil. The advantages of these preservatives are: the toxins are not very water soluble and therefore do not easily leach from the treated wood; the timber does not undergo dimensional changes; paints can be applied if a suitable solvent is used;

and colour can be added. The main problems are: the inflammability of some solvents and the high cost of solvents compared to water.

Although preservative treated wood is normally well protected against basidiomycete attack, in some situations, notably in soil or water contact, treated timber is subject to decay by soft-rot micro-organisms. This type of decay generally takes the form of a softening of the wood surface with little or no internal decay. The decay gradually progresses through the wood substance. Preservative treated wooden posts partially embedded in soil generally only suffer such decay at and below the ground line with the above ground portion remaining largely unaffected.

Nitrogen and wood decay

The decay of wood by micro-organisms may be inhibited by deficiencies of essential nutrients.

Carbon, hydrogen and oxygen, the three most important macronutrients (on a weight basis) to micro-organisms, are all present in large quantities in all plant material. Nitrogen is the next most important macro-nutrient, being required as a major constituent of structural proteins, enzymes, nucleic acids and amino acids. Most herbaceous plant litter contains between 1 and 5% nitrogen (Cowling and Merrill, 1966) and microbial decomposition of such

litter in soil is rapid. However, the nitrogen content of wood rarely exceeds 0.2% $\frac{w}{w}$ and is often below 0.1% $\frac{w}{w}$ (Merrill and Cowling, 1966). Therefore nitrogen availability is of critical importance in the decay of wood: the low levels present in wood limit rates of microbial growth and enzyme production.

Basidiomycete fungi which decompose wood have evolved an adaptive physiology allowing them to grow in and decay wood without supplementary nitrogen (Levi and Cowling, 1969). Whereas most fungi and bacteria have a nitrogen content of 3 to 6% $\frac{w}{w}$ and 8 to 15% $\frac{w}{w}$ respectively, basidiomycetes decaying wood may contain as little as 0.8% $\frac{w}{w}$ nitrogen (Cowling and Merrill, 1966). This small amount of nitrogen is distributed mainly to the enzyme mediated metabolic pathways which include the production of cellulolytic and in some cases lignolytic enzymes. It has also been suggested (Cowling and Merrill, *op cit*) that basidiomycete fungi reabsorb nitrogen from autolysing dead mycelium.

In contrast to the basidiomycetes, soft-rot fungi generally require more nitrogen than that present naturally in wood in order to decompose it (Levi and Cowling, 1969; Butcher and Drysdale, 1974). They only become actively cellulolytic when the carbon to nitrogen ratio of wood falls below 200:1, equivalent to a nitrogen concentration of about 0.2% $\frac{w}{w}$ (Levi and Cowling, *op cit*).

Therefore nitrogen inputs to wood are clearly required before soft-rot decay occurs and since the nitrogen concentration of wood undergoing soft-rot decay in soil contact is normally well above the 0.2% "threshold" proposed by Levi and Cowling (King, Oxley and Long, 1976), nitrogen inputs to wood are clearly involved in the decay process.

Several mechanisms by which the nitrogen content of wood in soil might be enhanced to allow soft-rot decay have been postulated. Levy (1968) proposed that water moved through wooden fence posts in soil due to evaporation at the top of the post. Baines and Levy (1979) demonstrated movement of water through stakes (termed "wick action") with one end in a sealed jar of water and proposed that such movements of soil water through wood in soil might carry soluble nitrogenous salts into the wood, thus elevating the wood nitrogen content. Uju, Baines and Levy (1981) and Baines (1983) have also demonstrated that wick action can lead to nitrogen uptake by wooden stakes emplaced in sterilised nitrogen augmented soil. Sharp and Millbank (1973), Levy *et al* (1974) and Baines and Millbank (1976) also demonstrated nitrogen fixation by bacteria in wood under anaerobic conditions.

King (1975) found increases in the nitrogen concentration of totally buried wood blocks which had been colonised by micro-organisms and concluded that these nitrogen increases were largely in the form of micro-organisms entering wood from soil. Waite and King (1979) found that the amount of nitrogen present as nitrate in buried wood blocks was negligible. They also found a constant correlation between increases in the nitrogen concentration of wood and levels of weight loss by soft-rot decay.

Pure culture studies by King and Waite (1979) and King, Henderson and Murphy (1980) have respectively shown that fungi and bacteria can contribute a significant amount of nitrogen to wood. King and Waite (1979) and Waite and King (1980) suggested that decaying wood in soil was undergoing a continuous "invasion" by micro-organisms and that biotic transport of nitrogen into wood by micro-organisms was the main source of the nitrogen increases they observed. Thus micro-organisms entering wood emplaced in soil might themselves produce threshold nitrogen or inoculum levels above which soft-rot decay can occur, with continued microbial invasion of the wood and hence further nitrogen increases after decay has been initiated.

Lignin may also play a role in the nitrogen economy of wood decay in soil. King, Mowe, Smith and Bruce (1983)

observed an increase in the lignin nitrogen content of wood during decomposition in soil. This increase in lignin nitrogen with time also occurs during the decomposition of forest litter (Berg, 1978) and is normally attributed to adsorption of ammonium ions released from breakdown of plant proteins on to lignin residues (Nommick, 1965). Such lignin bound ammonium ions in wood could be released from cation exchange sites in response to a fall in the ammonium content of the surrounding wood and could thus act as a reservoir of nitrogen for micro-organisms decaying wood.

Chemostimulation of micro-organisms by wood

Mowe, King and Senn (1983)have shown that certain soft-rot microfungi grow chemotropically towards wood, apparently attracted by volatile compounds emanating from the wood. These responses are not affected by the presence of CCA in the wood. Further studies by Mowe (1983) have shown that some bacteria common in soil move chemotactically towards aqueous wood extracts. Soluble nutrients leaching from wood into soil may also stimulate stasis release and spore germination in soil micro-organisms (Smith, 1980). Such chemostimulation of soil microflora by wood emplaced in soil might provide a mechanism for a continuous movement of micro-organisms into wood, as postulated by King *et al*, leading to the observed increases in nitrogen concentration both prior to and during soft-rot decay.

King, Oxley and Long (1974) showed that during normal drying procedures, soluble nutrients in wood migrate to evaporative surfaces, producing nutrient rich surface profiles which may have nitrogen concentrations close to or in excess of 0.2% $\frac{w}{w}$. Further studies (King, Oxley and Long, 1976) showed that the degree of soft-rot cavity formation was greater in spruce wood from the surfaces of dried planks rich in soluble nutrients than in wood from matched ring groups taken from beneath the plank surface. Waite and King (1979) found that such "surface nutrients" accelerated both the rate of decay and the rate of increase in nitrogen concentration in hardwoods and a softwood during decay in soil. Thus surface nutrients can act as an early stimulus to the decay process and could contribute significantly to the failure of preservative treated timber in soil contact and since many tropical hardwoods have a high soluble nutrient content, such nutrients could partially account for the premature failure of CCA treated hardwoods in tropical areas.

Copper, chrome, arsenic (CCA) preservative

CCA is widely used to treat building timber, fencing for agricultural use and roadways, wood used in horticulture and agriculture e.g. in vineyards, transmission poles, mining timber and timber used in low cost housing (Wallace, 1968). This preservative was first patented in

India by Kamesam (1933) and was known as "Ascu". It comprised a mixture of potassium dichromate, copper sulphate and arsenic pentoxide. Other CCA formulations were subsequently introduced elsewhere. They fall into three broad types using different proportions of the same constituents: Type I (or A) containing approximately 8.4% copper, 19.5% chromium and 6.2% arsenic by weight, represented by Ascu and the American "Greensalt"; Type II (or C) containing approximately 8.1% copper, 15.9% chromium and 14.6% arsenic, represented by "Celcure A" and "Tanalith C" and Type III (or B) containing approximately 11.9% copper, 13.8% chromium and 22.5% arsenic represented by "Boliden K33". CCA employed in Britain is generally Type II or C and the current British Standard (BS4072, 1974) includes a formulation of this type comprising 45% $K_2Cr_2O_7$, 35% $CuSO_4.5H_2O$ and 20% $As_2O_5.2H_2O$. The copper and arsenic are generally considered to be the toxic elements to fungi and insects respectively whilst the chromium plays an important role in the fixation of the preservative to wood.

Fixation of CCA to wood

Since CCA was devised as a preservative suitable for external uses, resistance of the toxic elements to leaching was a high priority. Leach resistance in

CCA is achieved by a chemical fixation of the preservative either directly to the wood substance or in the form of precipitates deposited in the wood cells.

Many aqueous leaching studies (Kamesam, 1933; Wilson, Tamblyn and McCarthy, 1955; Dunbar, 1962; Henshaw, 1979) have shown that CCA is highly resistant to leaching from wood but several studies (Kamesam, 1933; Henry and Jeroski, 1967; Fahlstrom, Gunning and Carlsson, 1967; Wallace, 1968; Smith and Williams, 1973b) have highlighted the importance of the composition of CCA on its leachability. These studies have shown that formulations corresponding to a Type II or C CCA preservative generally give minimal leachability of all three preservative elements and have confirmed that dichromate is important for the fixation of CCA to wood. As the amount of dichromate in the formulation is increased, the leachability of both copper and arsenic is reduced whilst the leachability of chromium, which is normally very low, suddenly increases as this element becomes present in excess. Smith and Williams, for example, found that CCA formulations must include at least 45% potassium dichromate before high fixation of copper and arsenic was achieved, whereas leachability of chromium, completely fixed when present in proportions smaller than 45% leached slightly above this figure.

Several workers have used results of leaching studies to predict fixation mechanisms for CCA in wood. Eadie and Wallace (1962) concluded that the majority of arsenic was fixed to wood in the form of chromium III arsenates with some copper arsenates present at high CCA loadings whilst copper was fixed either in the form of copper chromates or directly to the wood substance. Smith and Williams (1973b) found that leachability of arsenic from CCA treated wood was not influenced by the proportion of copper in the formulation. However, leaching losses of copper increased as the proportion of arsenic in the formulation increased. These authors concluded that copper and arsenic did not combine together in CCA treated wood and were fixed independently by reactions with chromium, with arsenic being fixed preferentially to copper. Their findings disagreed with those of Eadie and Wallace in that they considered that little of the copper was fixed directly to the wood substance.

Studies by Belford, Preston, Cook and Nevard (1957) and Belford, Myers and Preston (1958) using electron diffraction techniques suggested that copper and some other metal ions may be adsorbed in an ordered fashion on to the surface of cellulose microfibrils, possibly complexed to pentosans (Preston, 1961). Bayley and Rose (1960) however, proposed that copper ions react with cation-binding carboxylic acid groups of non-cellulosic constituents of wood. Bland (1963) further suggested

that copper ions reacted predominantly with lignin, binding with carboxyl and other groups. Michie (1961) showed Langmuir-type isotherm adsorption of copper by cellulose, the uptake of copper being proportional to the carboxyl content of the cellulose. This type of adsorption of copper could presumably also occur with acid groups of lignin. Eadie and Wallace (*op cit*) attributed partial fixation of copper to wood in the absence of chromium and arsenic to complexing of copper ions with either lignin or cellulose. These authors concluded that since the amount of copper fixed increased with increasing copper concentration in the treating solution, most fixation must be with cellulose microfibrils as proposed by Belford *et al*.

The fixation of CCA to wood has been studied in detail in a series of papers by Dahlgren and Hartford (1972a,b,c) and Dahlgren (1974, 1975a,b) and in later work by Pizzi (1981, 1982a,b,c). These studies show that the fixation process involves a complex series of chemical reactions but the studies of Pizzi disagree with the earlier studies in relation to the final products of fixation.

Dahlgren and Hartford and later Dahlgren alone studied pH changes in mixtures of CCA solutions and sawdust stored at constant temperature. The rate of fixation of chromium to wood was also determined by analysis of CCA treated sawdust leached at intervals

after treatment. The pH of the sawdust rose gradually to a maximum and then oscillated for several months. Dahlgren and Hartford (1972c) attributed the gradual rise in pH to proton consumption as a result of chromate reduction and the subsequent oscillations in pH to alternating release of protons by conversion of acid and tertiary copper arsenates to basic copper arsenate and consumption of protons due to further reduction of chromate to chromium (III) hydroxide. The authors considered that the final products of fixation were copper fixed to ion exchange sites on the wood and precipitated $CrAsO_4$, $CuHAsO_4$ and $Cr(OH)_3$. They also considered that the amount of dichromate in the formulation was of considerable importance in determining the final pH of the wood and hence the leachability of the preservative: excess chromium converted to $Cr(OH)_3$ should elevate the wood pH and hence improve preservative stability.

Pizzi studied interactions between chromium VI and model lignin and cellulose compounds: D-glucose, α-cellulose, guaicol or lignosulphonates and combinations of these. Further studies were undertaken of the reactions of the same model compounds with copper and chromium VI together and with CCA. Pizzi (1982c) proposed a reaction mechanism for CCA with wood: initially copper becomes fixed to cation exchange sites on wood and chromium (VI) is adsorbed by cellulose; some of the

copper gradually forms complexes with lignin and cellulose; chromium (VI) is reduced to chromium (III) on cellulose sites; $CuCrO_4$ is formed and complexes with guaicyl units of lignin; further chromium VI reduced to chromium (III) forms $CrAsO_4$ and complexes with lignin or precipitates on cellulose; $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} form complexes with lignin. The work of Pizzi largely agrees with the earlier work of Eadie and Wallace (*op cit*) who concluded that the copper was fixed mostly in the form of chromates whilst the arsenic was mostly in the form of chromium (III) arsenates.

Selective absorption of CCA

Commercial practice does not normally include chemical analysis of wood to check preservative retentions. Preservative loadings are predicted by measuring the weight of preservative solution taken up by wood during treatment. This method has also been widely adopted in scientific studies but Smith and Williams (1973b), Henshaw (1979) and King, Smith, Baecker and Bruce (1981) have shown that wood treated with CCA, on analysis, often contains higher concentrations of preservative elements than would be predicted from uptake values. Henshaw found that in some cases analytical figures exceeded uptake data by more than three times. Smith and Williams termed this effect "selective absorption" and attributed it to fixation and adsorption reactions

occurring during the impregnation process. Such reactions should lead to a reduction in the nominal concentrations of preservative elements in the preservative solution. Smith and Williams also pointed out that Langmuir adsorption of cations on acidic groups of wood, as described by Michie (*op cit*) should increase with increasing pH. Thus, as the proportion of acidic arsenic pentoxide in CCA formulations falls, there should be an increase in the selective absorption of copper. This was confirmed by their studies. Hager (1969) also observed better resistance of copper in wood to leaching when mixed with sodium dichromate rather than the highly acidic chromic acid and attributed this to more cation exchange fixation of copper in the presence of sodium dichromate than chromic acid.

Factors affecting the fixation of CCA to wood

The temperature and relative humidity during curing of CCA treated wood influence the rate of fixation of the preservative elements to the wood.

Hager (*op cit*) found that the leachability of copper and arsenic from CCA treated wood was reduced if the rate of drying during curing was reduced. Henshaw (*op cit*) also highlighted the importance of maintaining a high moisture content during the curing of CCA treated wood: maximum fixation of CCA in wood stored at 25°C and 83%

relative humidity was achieved in two weeks implying that fixation reactions proceed in the aqueous phase. The rate of fixation was also increased at elevated temperatures.

Studies by Eadie and Wallace (*op cit*) and Wilson (1971) have shown that the fixation of CCA to wood is influenced by treating concentration: the proportion of preservative elements leached from wood is reduced with increasing treating concentration.

Leachability of CCA from wood in service

Wallace (*op cit*) has pointed out that the degree of leaching of CCA from treated wood in service may be influenced by the size and species of timber and by the conditions of the soil, particularly its pH.

Purushotham and Tewari (1960) have shown in laboratory tests that the rate of leaching of CCA decreases with increasing specimen size. Becker and Buchmann (1966) and Wilson, Tamblyn and McCarthy (1955) found better fixation of CCA in softwoods than in hardwoods. However, Henshaw (*op cit*) found no significant difference between fixation of CCA in softwoods and hardwoods.

Although the toxic elements in CCA are well fixed to wood, none of the complexes or compounds formed during the fixation process are likely to be totally insoluble.

Fahlstrom, Gunning and Carlsson (*op cit*) observed that leaching losses of CCA still occurred at a low level even at the end of a fourteen day leaching period. McCarthy and Wilson (1957) observed an increase in losses of copper and arsenic during the latter part of a 128 day leaching period. They attributed this increase to slow reactions of the fixation products releasing acid and breaking down complexes. Therefore CCA treated timber exposed to water or moist soil for many years might undergo a gradual depletion of toxic elements and hence a reduction in toxicity.

The effect of the soil environment on the stability of CCA in wood has not been extensively studied. Narayanamurti and Purushotham (1956) found little loss of CCA from timber which had been in soil contact for periods of up to eight years. However, such factors as soil pH and microbial activity might have a considerable influence on the leachability of CCA. McCarthy (1959) has shown that CCA treated wood loses considerably more copper and arsenic when leached in an acid buffer than in distilled water (about 50% of total copper and up to 40% of total arsenic were lost during an acid leach whereas distilled water removed less than 3% of both these elements). Thus highly acidic soils might adversely affect the stability of CCA in wood buried in them. Levi (1976) has demonstrated that fungal presence may cause considerable solubilisation of CCA fixed to wood and since fungal

mycelium has been isolated from timber treated with high concentrations of CCA (Hulme and Butcher, 1977b) considerable detoxification of CCA treated wood emplaced in microbially active soils may occur.

The Effectiveness of CCA treated wood in soil contact

Many field tests have shown that CCA treated timber can perform successfully in soil contact for many years (Wallace, 1968; Davidson 1977a,b).

In temperate climates, the main source of timber is from the fast growing softwood conifers and these have generally performed well when treated with CCA. However in tropical countries and Australia, the majority of timber is of the hardwood type and such timber treated with CCA has frequently been shown to fail prematurely in soil contact (Tamblyn, 1973; Aston and Watson, 1976; Henningsson, 1976; Greaves, 1977) due to soft-rot attack.

Several theories have been proposed to explain the poor performance of CCA treated hardwoods against soft-rot when compared to softwoods.

Aston and Watson (1976) drew attention to the reported better fixation of CCA in softwoods than some hardwoods (Wilson, Tamblyn and McCarthy, 1955; Nicholson and Levi, 1971). Leaching losses of CCA from some hardwoods, under

heavy tropical rainfall conditions might result in reduced toxicity of such hardwoods in service.

Poor macrodistribution of CCA may occur in some species of hardwoods during treatment (Greaves, 1972; 1974; Dickinson, 1974; Dickinson, Sorkoh and Levy, 1976) leading to zones of the wood remaining untreated. Butcher (1978) considered, however, that poor macrodistribution of CCA could not account for the high susceptibility of CCA treated hardwoods to soft-rot decay since many hardwoods treat well with wood preservatives (Hulme and Butcher, 1977a) and Hulme and Butcher 1977b found no correlation between treatability of wood with CCA and its susceptibility to soft-rot.

Greaves (1974), Dickinson (1974) and Dickinson, Sorkoh and Levy (1976) found lower cell wall loadings of CCA in hardwoods than in softwoods and thus proposed that soft-rot susceptibility of CCA treated hardwoods may be due to poor microdistribution of toxic elements in the wood. CCA penetrating hardwoods through vessels and wood cell lumens may not readily penetrate the cell wall to confer protection on the cellulose rich S_2 layers. Chou, Chandler and Preston (1973) found that CCA does readily penetrate the cell walls of softwood tracheids thus providing a possible explanation for the better performance of CCA treated softwoods. Hulme and Butcher (1977a) also found a twofold difference in cell wall

loadings of CCA between hardwoods and softwoods but this was small in comparison to the forty-fold difference observed by Dickinson, Sorkoh and Levy (1976). Butcher (1978) considered that such a large difference was likely to be due to poor macrodistribution whereas the much smaller difference observed by Hulme and Butcher might be due to the ratio of lumen volume to cell wall volume being much lower in hardwood fibres than in softwood tracheids.

Greaves (1974) and Hulme and Butcher (1977a) have observed an imbalance of preservative elements in the cell walls of hardwood fibres. Since CCA effectiveness may be influenced by variations in the proportions of toxic elements (Smith and Williams, 1973a), preservative imbalance could significantly affect the performance of CCA treated hardwoods.

Hulme and Butcher (1977c) proposed that the susceptibility of preservative treated woods to soft-rot decay is determined by the natural decay susceptibility of the untreated wood. Thus, softwoods, which are generally not highly susceptible to soft-rot attack even in the untreated state, only require small additions of preservatives such as CCA to confer complete protection, whereas hardwoods, which are generally decay susceptible, will require considerably more preservative in order to ensure complete protection. Hulme and Butcher found it

possible to protect hardwoods in laboratory studies by the use of very high loadings of CCA or by the use of ammoniacal copper arsenate which contains considerably more copper than CCA at any given salt concentration.

Butcher and Nilsson (*op cit*) related the performance of CCA treated wood to its lignin content. They hypothesized that if much of the copper in CCA was fixed to lignin in the form of copper chromates, as suggested by Pizzi (1982c), such lignin bound CCA might mask initiation sites in the S_3 wall for soft-rot cavity formation. They further hypothesized that since softwoods generally contain more lignin than hardwoods softwoods might bind enough CCA to mask all initiation sites whereas hardwoods might never bind enough CCA to mask all such sites and therefore cannot be completely protected. Thus, in practice, the only way to confer complete protection on some low lignin hardwoods with CCA might be to use very high loadings of CCA resulting in high concentrations being deposited in the cell walls.

Effects of nutrients on CCA toxicity

Henningsson (1976) has shown that microbial tolerance of copper and arsenic in CCA treated wood is influenced by nitrogen availability. Since concentrations of soluble nutrients at wood surfaces cause elevated nitrogen levels (King, Oxley and Long, 1974) Oxley, King and Long (1976) have suggested that such nutrients at the surfaces

of preservative treated wood might influence the toxic thresholds of wood preservatives in soil with respect to soft-rot decay at the wood/soil interface. The toxic threshold is defined as the concentration of preservative required to confer complete protection on a piece of wood for any specified period of exposure to decay organisms.

King, Smith, Baecker and Bruce (*op cit*) have shown that the toxic thresholds of CCA in treated lime are elevated in the presence of surface nutrients. These authors noted that although CCA depressed the rate of increase in nitrogen concentration in wood during soil burial, it did not prevent such increases. The presence of surface nutrients accelerated nitrogen inputs to CCA treated wood in a similar manner to untreated wood (King, Oxley and Long, 1976; Waite and King, 1979). King, Smith, Baecker and Bruce (*op cit*) postulated that nitrogen inputs to CCA treated wood in soil were due to a "sacrificial colonisation" of the wood by micro-organisms leading to the establishment of nutrient levels which would allow decay to proceed. Such microbial colonisation of CCA treated wood could be a consequence of a chemotropic growth of soil fungi towards such material (Mowe, King and Senn, *op cit*). King, Mowe, Smith and Bruce (1981) suggested that there is a constant "biotic connection" of fungal mycelium between decaying CCA treated wood and soil. Translocation of nitrogen from

soil into wood could occur through this mycelial connection.

Smith (1980) identified two stages in the decay of CCA treated wood in soil: firstly, the induction phase which was the period before measurable decay of the wood was observed; and secondly the decay phase which was the period during which a 100% reduction in tensile strength occurred. The length of both these phases increased with increasing CCA concentration but decay did eventually occur even in wood treated with very high concentrations of preservative. Smith considered that the length of the induction phase was determined by the amount of unfixed CCA preservative leaching into the soil. King, Smith, Baecker and Bruce (*op cit*) observed that lime treated with CCA to a retention of 16 kg/m^3 which did not decay showed no increase in nitrogen content, indicating that no micro-organisms had entered the wood from the soil. This suggests that CCA may have leached out of the wood in quantities sufficient to kill micro-organisms in the adjacent soil.

If high concentrations of CCA in wood do indeed only increase the lengths of the induction and decay phases, as suggested by Smith, it seems that decay of CCA treated wood in soil is inevitable. Therefore permanent protection of timber by CCA alone may be impossible.

Ammoniacal copper arsenate

Other water-borne preservatives besides CCA are used for the protection of timber for external uses. However, none of these preservatives, outlined earlier, are used as universally as CCA.

In North America, another group of preservatives, known collectively as "Ammoniacal wood preservatives" are extensively used. These preservatives, originally patented by Gordon (1940), commonly comprise the toxic cations copper and/or zinc and the toxic anions arsenate or borate dissolved in aqueous ammonia solution. They may also include other anions such as carbonate or acetate to improve the water-repellency properties of the treated timber.

The most commonly used ammoniacal preservative is ammoniacal copper arsenate (ACA). This preservative is made up from copper oxide or basic copper carbonate and arsenic pentoxide dissolved in ammoniacal solution. Some formulations also include small amounts of ammonium acetate or bicarbonate. Most formulations contain approximately equal weights of copper and arsenic oxides. The well established "Chemonite" preservative used in the United States since 1935, is an example of this type of preservative. It contains copper, arsenic and ammonium acetate in aqueous ammonia (Gordon, 1947) and although the arsenic is originally added in the form of arsenite,

this anion is oxidised to arsenate during preparation of the preservative (American Wood Preservers Association, 1975).

ACA has potential advantages over CCA as a preservative for use in timber in soil contact. Firstly, an ACA solution contains approximately four times as much copper by weight as a CCA solution of the same salt concentration. Therefore, ACA can be used to achieve very high loadings of the fungicide copper in timber. This could be of considerable significance in the protection of decay susceptible hardwoods as demonstrated in laboratory studies by Hulme and Butcher (1977c).

A second advantage of ammoniacal preservatives over other water-borne preservatives is that the ammonia may improve preservative penetration of the wood. Clarke and Rak (1976) have shown that white spruce absorbs ammoniacal solutions faster than water. Ammonia is known to cause swelling of cellulose and may dissolve fats, waxes, resins and polygalacturonic acids (Hulme, 1979). Solutions of copper in ammonia are also capable of dissolving cellulose. Thus, penetration of ACA into wood may be significantly faster than that of neutral or acidic preservatives. This factor may reduce the risk of poor macrodistribution of the toxic elements of ACA in treated timber and the swelling or dissolution of cellulose by the cuprammonium solution should lead to complete penetration of wood cell walls, thus reducing

micro-distribution problems (Hulme, 1979). Ammoniacal preservatives may be particularly useful in the treatment of refractory wood species such as spruce and douglas fir, both commonly cultivated for use as external timber in Europe and North America. Spruce is currently the predominant wood type grown in Britain for timber production.

Although the fixation of ACA to wood has not been extensively studied, it is thought to be due to precipitation of water insoluble copper arsenates as the ammonia evaporates during curing. Hulme (*op cit*) quotes a Russian study by Kuperman, Orlov, Krutitskaya and Trushkina (1955) which showed that in the absence of wood, loss of ammonia leads to the formation of complexes which vary in the ratio of metal to arsenic oxide. However, in wood, cuprammonium ions may complex with carboxylic acid groups of lignin or with hydroxyl groups of cellulose (Vazirani and Narwani, 1969). Therefore when ACA reacts with wood, there is some free arsenic left over after all copper has been precipitated and whilst the copper is generally very well fixed to wood, considerable amounts of arsenic may be lost during aqueous leaching studies (Rak, 1976; Wilson, Tamblyn and McCarthy, 1955; McCarthy and Wilson, 1957).

Service data on ACA treated timber in soil contact has shown that the preservative is effective (Fritz, 1947; Davidson, 1977a; 1977b). However, Ruddick (1979) has

shown that the nitrogen content of ACA treated pine and spruce can be considerably higher than that of untreated wood even after long periods of uncovered storage outdoors. This extra nitrogen, if present in an available form, could act as a source of nitrogen to micro-organisms invading ACA treated wood in soil and thus stimulate decay of the preserved wood in a similar way to concentrations of soluble nutrients in CCA treated wood, as observed by King, Smith, Baecker and Bruce (*op cit*). Aqueous ammonia leaching from ACA treated wood into soil might lead to a chemostimulation of the soil microflora and thus stimulate the microbial invasion of wood.

The Ecology of Wood decay in soil

King, Mowe, Smith and Bruce (*op cit*) stressed the importance of studies of the total ecology of wood and soil: timber emplaced in soil represents a source of litter and thus becomes a part of the soil ecosystem. It is therefore unwise to consider wood decay in soil merely in terms of processes occurring within the confines of the wood substance.

Soluble nutrients, volatile compounds or preservative elements emanating from preservative treated wood into soil may have a profound effect on the soil microflora and the response of micro-organisms in the soil to these compounds influences the performance of the wood. The

effect of the soil itself and its microflora on preservative stability and decay rates may also be considerable. The micromorphology of the wood and chemical constituents such as lignin may ultimately determine how rapidly decay develops in treated timber once the micro-organisms have entered it.

Aims of the current studies

1. The presence of concentrations of soluble nutrients have previously been shown to increase the toxic thresholds of CCA in the hardwood lime when buried in soil. Such nutrients might similarly influence the toxic thresholds of CCA in softwoods. Soluble nutrients might accelerate decay rates of CCA treated wood in soil as a result of stimulating the transfer of microbial biomass to wood, leading to the early establishment of threshold nutrient or microbial levels required for decay. The presence of soluble nutrients might also decrease the stability of CCA in the wood, leading to the loss of preservative elements to the surrounding soil.

An ex tensive 18 week burial experiment was undertaken to determine the effects of concentrations of soluble nutrients on the susceptibility of a CCA treated hardwood and softwood to decay in soil and to determine losses of CCA from the wood to the soil. The nitrogen dynamics of decay were also followed to determine the effect of soluble

nutrients on the rates of microbial invasion of CCA treated woods.

2. The experiment described above demonstrated some losses of preservative elements from CCA treated wood in soil. Such losses might be caused by a combination of several factors: incomplete fixation of CCA to wood, leading to the loss of the unfixed, soluble portion to the soil by aqueous leaching; solubilisation of CCA previously fixed to wood by soluble components of soil such as humic acid, leading to increased leach losses; solubilisation of CCA by fungi and bacteria present in the soil, also leading to increased leach losses.

Experiments were undertaken to determine the leachability of CCA from treated wood in distilled water, an aqueous soil extract and an aqueous soil extract containing micro-organisms to determine the possible effect of each factor on the leachability of preservative elements.

3. The residual extra nitrogen present in ACA treated wood might influence the toxicity of the preservative when used in wood in soil contact in a similar way to soluble nutrients: soluble nitrogen might stimulate microbial invasion of ACA treated wood and insoluble nitrogen might also act as a source of nutrients during decay.

A further burial experiment was undertaken to determine the effect of the extra nitrogen in ACA treated wood on the toxic thresholds of the fungicide copper: toxic thresholds of copper were compared with those for similar wood species treated with CCA calculated from the data from Chapter 2. The nitrogen economy of decay of ACA treated wood in soil was also studied to determine the influence of the extra nitrogen present on the rate of the microbial invasion of such wood.

4. Lignin might play an important role in the fixation of timber treated with CCA. As a source of cation exchange sites, it may be an important site for the fixation of copper and chromium ions to wood. It may also be important in the fixation of chromate anions to wood (Pizzi, *op cit*) and hence in the fixation of CCA generally.

Lignin may also play an important role in the decay of wood, not only as a barrier to decay of cellulose and hemicellulose by non-lignolytic micro-organisms, but also as a potential store for nitrogen released during the decay process. Fixation of nitrogen in the form of ammonium ions to cation exchange sites on lignin might be particularly important in ACA treated wood.

Experiments were undertaken to examine the role of lignin and cellulose in the fixation of CCA to wood and to

examine the role of lignin in the nitrogen economy of decay of untreated and ACA treated wood in soil.

CHAPTER 2

THE EFFECT OF SURFACE NUTRIENTS ON THE DECAY SUSCEPTIBILITY OF CCA TREATED WOOD IN SOIL

2.1 Introduction

CCA treated hardwoods in service in soil contact have frequently failed prematurely due to soft-rot, particularly in tropical and sub-tropical environments (Tamblyn, 1973; Aston and Watson, 1976; Greaves, 1977). The poor service record of CCA treated hardwoods in tropical regions may be due, in part, to the high rainfall and temperatures increasing microbial activity in soil, decay rates and leaching of toxic elements from wood. However, even very high retentions of CCA (24 kg/m^3) do not provide complete protection to eucalypt in these conditions (McNamara, Greaves and Triana, 1981).

Several theories (Chapter 1) have been postulated regarding the poor performance of CCA treated hardwoods when compared with softwoods: poor macrodistribution of toxic elements in CCA treated hardwoods (Greaves, 1972; 1974; Dickinson, 1974; Dickinson, Sorkoh and Levy, 1976); poor microdistribution of the toxic elements in CCA treated hardwoods leading to inadequate protection of cell walls (Greaves, *op cit*; Dickinson, *op cit*; Dickinson, Sorkoh and Levy, *op cit*); an imbalance of the toxic elements in the cell walls of hardwood fibres (Greaves, *op cit*; Hulme and Butcher, 1977a); the need for higher concentrations of CCA to overcome the high natural decay susceptibility of untreated hardwoods when compared to untreated softwoods

(Hulme and Butcher, 1977c) and the incomplete protection by lignin bound copper of low lignin content, decay susceptible hardwoods when compared to softwoods (Butcher and Nilsson, 1982). Early failure of CCA treated hardwoods may be due to a combination of all of these factors.

CCA treated softwoods have generally performed well in soil contact situations (Davidson, 1977a; b). However, recent experience in New Zealand has proved that this is not always the case: pine posts treated to above the New Zealand specification of 6.74 kg/m^3 with CCA and subsequently used in horticultural land have failed after eleven to twelve years (Butcher, 1984). Similarly treated pine posts in adjacent pastoral land have shown no signs of early failure and have an expected service life in excess of thirty years. This decay problem is not specific to soft-rot since all of the common types of decay micro-organism have been isolated from the failed CCA treated pine posts (Drysdale and Hedley, 1984). Although the major decay type present in the posts has been soft-rot, the failures have generally been caused by brown-rot fungi, with evidence of white-rot and bacterial (tunneling and cavitation) attack. Comparisons of CCA concentrations for above and below ground portions of the failed posts (Hedley, 1984) have shown that wood in contact with soil has lost preservative elements, especially chromium and arsenic. These losses may be due, in part, to the high soil water electrolyte concentrations produced by added fertiliser.

The soil pH of 5.2 - 6.8 (Drysdale, 1984) would not alone be expected to account for such losses. Analysis of failed pine posts with electron probe micro-analysis (Butcher, 1984) has shown that preservative losses appear to be from the S_2 layers of tracheids below ground, particularly adjacent to zones of fungal attack. Such losses could be caused by fungal solubilisation of CCA observed by Levi (1976) with losses being accelerated by the large microbial flora of the highly fertile soil adjacent to the wood. The low chromium/arsenic ratio of the CCA formulations currently used in New Zealand may have contributed to the early failure of pine posts since recent experimental work has shown that as the ratio of chromium to arsenic in CCA treated pine is reduced, both leach resistance (Plackett, 1984) and preservative effectiveness (Hedley, 1984) are reduced. Butcher (1984) has pointed out that the highly fertile soils support a large inoculum of a broad spectrum of decay micro-organisms. Thus, the posts emplaced in the soil are subjected to an extremely hazardous environment where decay is inevitable unless preservative retentions are greatly increased above normal specifications.

Prior to the studies of losses of toxic elements from pine posts in New Zealand there had been little previous reported work on loss of CCA from treated wood in soil. Smith (1980), using laboratory test results, considered

that leaching losses of toxic elements from CCA treated wood in soil govern the length of the induction phase prior to the onset of decay and that decay cannot occur while the concentration of CCA in soil adjacent to wood is high enough to inhibit microbial growth. Therefore decay of the wood will only commence once the level of preservative losses diminishes to a point where soil micro-organisms can exist at the wood/soil interface. Smith's theory suggests that decay of wood treated with any concentration of CCA is inevitable in soil once leaching losses cease, although the CCA concentration in the wood may determine the decay rate. There is no doubt that very high loadings of CCA (over 40 kg/m^3) do not prevent soft-rot decay in CCA treated eucalypt poles (Leightley and Norton, 1983).

Previous studies on the permanence of CCA in wood have concentreated on the level of leaching losses during aqueous leaching experiments (Kamesam, 1933; Wilson, Tamblyn and McCarthy, 1955; Henshaw, 1979). These studies confirmed that CCA is highly resistant to leaching from wood in water. However, in all cases, small losses of toxic elements were observed. These losses may partially represent gradual solubilisation of preservative elements previously fixed to wood but the fact that most losses occur during the early leaching periods suggests that most of the losses result from leaching of unfixed preservative from the wood. The actual amount of copper,

chromium and arsenic lost from CCA treated wood during leaching is likely to increase with increasing treating concentrations, thus possibly accounting for the lengthening of the induction phase, as the CCA treating concentration increases (Smith, *op cit*).

The losses of unfixed CCA from treated wood in soil may be supplemented by other effects: fungi present in soil adjacent to wood or killed by the action of soluble CCA may solubilise further CCA from the wood (Levi, *op cit*); highly acidic conditions may directly reduce the stability of the CCA/wood complexes (McCarthy, 1959) and hence acidic soils may cause increased leaching losses of CCA; high ionic compositions in soils may also increase CCA losses from wood (Hedley, 1984).

It is clear that no CCA treated wood is completely immune to decay in soil contact and factors such as preservative stability and soil type as well as wood type partially determine the service life of CCA treated timber in soil.

Nutrient availability in the wood and soil may also influence preservative effectiveness. Nitrogen is considered to be the major limiting nutrient to micro-organisms decaying untreated wood (Merrill and Cowling, 1966) and Henningsson (1976) has shown that the toxic thresholds of copper and arsenic in CCA treated wood increase as nitrogen content is increased. High nitrogen concentrations

in fertile soils around CCA treated wood may influence preservative performance: soluble nitrogen may enter posts by wick action, as described by Uju, Baines and Levy (1981) or nitrogen may be actively translocated into the wood by invading micro-organisms as suggested by Waite and King (1980). Both of these processes might lead to accelerated nitrogen increases in wood in very fertile soils and may provide a partial explanation for the premature failure of CCA treated pine posts in horticultural soils in New Zealand.

Concentrations of nitrogenous and other soluble nutrients have been shown to accumulate at wood surfaces during drying (King, Oxley and Long, 1974). King, Smith, Baecker and Bruce (1981) have shown that such nutrient rich surface profiles influence both the toxic thresholds and the rate of nitrogen increase in CCA treated lime. Also, the toxic threshold of CCA in treated kempas, a hardwood with a high soluble nutrient content, was reduced when wood blocks were leached prior to preservative treatment.

Waite and King (1979) noted that in untreated lime the effect of surface nutrients on decay rates and nitrogen increases was most marked in the early stages of an eighteen week burial period. However, the study by King, Smith, Baecker and Bruce (*op cit*) included only one sampling interval at fourteen weeks and it was therefore not possible to study the nitrogen dynamics of decay during the early

stages of the burial of the CCA treated wood. The study also did not include a softwood: since the rate of decay of untreated pine is influenced by surface nutrients (King, Oxley and Long, 1976), such nutrients may also influence the toxic thresholds of CCA treated pine.

Surface nutrients, if present in CCA treated wood, may also influence preservative stability. It is possible that components of the surface nutrients, particularly amino acids, may complex CCA, but especially copper and chromium, during treatment rather than these elements becoming fixed to insoluble wood substance. Such CCA complexed to soluble nutrients might be susceptible to leaching from wood and may not be available to protect the wood substance against microbial attack. Also, if a fungal presence in wood increases solubilisation of CCA as described by Levi (*op cit*), a stimulation of microbial invasion of CCA treated wood by surface nutrients, leading to a large fungal biomass in the wood, might cause leaching losses of CCA from wood.

A large scale laboratory-based wood block soil burial programme was undertaken to study the influence of surface nutrients on the performance of CCA treated wood in soil. The procedure adopted for this study involved the burial of nearly one thousand small (10 x 10 x 5 mm) wood blocks, either CCA treated or untreated, in non-sterile soil contained in plastic boxes. Although such small block soil burial systems do not give results directly comparable

with large scale service material, they provide a convenient method for the rapid evaluation of the performance of treated wood. They may be considered to provide an accelerated representation of the actual process occurring at the surface of service material.

The standard procedure for the preservative treatment of wood blocks for laboratory-based decay-susceptibility experiments (BS6009, 1982) involves soaking the blocks for two hours in the preservative solution. The placement of small wood blocks in preservative solution for such a long period leads to considerable losses of these nutrients from the blocks due to leaching (A.A.W. Baecker, unpublished data). King, Smith, Baecker and Bruce (1981) demonstrated that although selective absorption of copper and chromium by small wood blocks did increase slightly between five and one hundred and twenty minutes of soaking in CCA solution during impregnation, uptake of preservative solution did not increase significantly after five minutes. It was therefore decided that all blocks used in this burial experiment should be allowed to soak in the CCA solution for only five minutes in order to minimise losses of surface nutrients.

The specific aims of the study described here were to determine:

1. The effect of surface nutrients on the toxic thresholds of CCA in both a hardwood and a softwood in soil.

2. The effect of surface nutrients on the rate of microbial invasion of a CCA treated hardwood and softwood in soil, as measured by increases in the nitrogen concentration of the wood.

3. The magnitude of any losses of CCA from treated hardwoods and a softwood in soil contact.

4. The effect of surface nutrients on the level of preservative losses occurring from a CCA treated hardwood and softwood in soil.

5. Whether copper, chromium and arsenic are absorbed selectively by wood from treating solutions during impregnation with CCA and if so to determine selective absorption ratios for these preservative elements at a range of CCA treating concentrations.

2.2 Materials and Methods

The preparation of the test wood blocks, their exposure to soil and subsequent exhumation and drying were undertaken by A.A.W. Baecker.

2.2.1 Preparation of Wood Blocks

Three wood species were used: the hardwoods Lime (*Tilia vulgaris*, Hayne) and Beech (*Fagus sylvatica*, L) and the softwood pine (*Pinus sylvestris*, L).

Pine and lime trees were felled locally during 1978. 1 metre bolts were removed at breast height and quartersawn into planks approximately 70 mm thick. The planks were wrapped in polythene and stored at -18°C until required.

The planks were subsequently dried at 40°C in a fan oven for two weeks and then flat sawn to produce sapwood strips consisting of rings 3 to 15 (measured from the cambium) and rings 16 to 30 representing outer and inner sapwood zones respectively. The sapwood zones were further flat sawn to produce 10 mm strips which were then sawn radially to produce strips 5 mm thick. These strips were then sawn transversely to produce blocks 10 x 10 x 5 mm with large (10 x 10 mm) radial faces and small (10 x 5 mm) tangential and transverse faces. Strips from the evaporative surfaces of the planks produced

blocks with high concentrations of soluble nutrients (referred to henceforth as "Redistributed Soluble Nutrient" (RSN) blocks). Strips from beneath the plank surfaces produced matched ring group "centre" wood blocks low in soluble nutrients.

Beech blocks without high concentrations of soluble nutrients were supplied by the Biodeterioration section, Princes Risborough Laboratory, Buckinghamshire. They were of identical dimensions to the lime and pine blocks and also had large (10 x 10 mm) radial faces. These blocks were also prepared from ring groups 3 to 30 of the sapwood zone measured from the cambium.

All prepared wood blocks were labelled with Indian ink, dried in an oven at 102 ± 2°C for 3 hours, placed in a dessicator to cool and then weighed.

2.2.2 Preparation of preservative solutions

CCA solutions (Type C) were prepared according to BS4072 (1974) using Analar grade reagents dissolved in distilled water. Solutions of 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, 2.5 and 3.0% $\frac{W}{V}$ CCA were prepared by dissolving $K_2Cr_2O_7$, $CuSO_4.5H_2O$ and $As_2O_5.5H_2O$ in distilled water. ($As_2O_5.5H_2O$ was used in preference to the dihydrate specified in the standard due to the more rapid dissolving of the pentahydrate in water.)

The composition by weight of the salts in the CCA was: 43.40% $K_2Cr_2O_7$, 33.76% $CuSO_4.5H_2O$ and 22.85% $As_2O_5.5H_2O$ (equivalent to 45% $K_2Cr_2O_7$, 35% $CuSO_4.5H_2O$ and 20% $As_2O_5.2H_2O$).

In order to confirm the correct formulation of solution, samples were diluted and analysed for copper, chromium and arsenic content on an atomic absorption spectrophotometer by a standard additions method (described later).

2.2.3 Preservative treatment of wood blocks

The numbers of blocks of each wood type treated with each CCA treating concentration are shown in Table 2.1. Numbers of untreated control blocks are also included.

Table 2.1

Numbers of blocks of each wood type treated with each concentration of CCA

Wood Type	CCA Treating Concentration (% $\frac{w}{v}$)								
	Untreated	0.25	0.50	0.75	1.0	1.5	2.0	2.5	3.0
Pine Centre	24	24	24	24	24	24			
Pine RSN	24	24	24	24	24	24			
Beech	36		36		36	36	36	36	36
Lime Centre	36		36		36	36	36		
Lime RSN	36		36		36	36	36	36	36

Wood blocks were impregnated according to BS6009 (1982) except that the blocks were only soaked in the preservative solutions for five minutes to minimise losses of soluble nutrients.

All blocks to be treated with the same preservative concentration were placed in a 1 litre beaker in a vacuum dessicator with their radial faces in the horizontal plane. The blocks were weighted down using plastic mesh and lead weights. A vacuum was then drawn in the dessicator and held for 15 minutes. The preservative solution was then drawn into the beaker within the dessicator until the blocks were completely covered. Air was then admitted to the dessicator to restore atmospheric pressure and the beaker containing the blocks and preservative solution removed from the dessicator.

The blocks were allowed to soak in the preservative solution for five minutes after which time the blocks were lifted out of the solution, blotted lightly with tissue paper to remove excess preservative solution and then weighed individually to determine block mass after impregnation. The liquid uptake of each block was subsequently calculated by subtracting the initial dry weight from the treated weight and the theoretical copper, chromium and arsenic retention calculated as a % $\frac{W}{V}$ of the initial dry weight of the blocks using the measured densities of the preservative solutions.

2.2.4 Curing of wood blocks

The wet, treated blocks were transferred to a glass vessel and placed on plastic mesh on their narrow faces, care being taken to ensure that the blocks were not touching one another. Further layers of mesh and blocks were then placed above the first. The vessel was then sealed for two weeks. During the third week the cover of the vessel was progressively opened and at the start of the fourth week the cover was completely removed.

Throughout this four week curing period, the blocks were turned twice per week.

After curing, six blocks of each wood type at each treating concentration were set aside in compartmented plastic repli-plates prior to analysis as unburied controls.

2.2.5 Preparation of soil

Unfertilised topsoil with no recent biocide application was collected from the Scottish Crop Research Institute (Invergowrie), brushed through a 5 mm sieve to remove larger stones and then shaken through a 2 mm sieve to remove finer grit. The soil was then stored in large plastic bins covered with loose-fitting lids until required. The water holding capacity (WHC) and moisture content were calculated according to the method of Savory and Carey (1972) immediately prior to use in the experiment.

2.2.6 Burial of wood blocks in soil

Wood blocks were buried in soil for periods of up to 18 weeks. Lime and beech blocks were sampled after 3, 6, 9, 12 and 18 weeks of burial in soil and pine blocks were sampled after 6, 12 and 18 weeks. Six replicate blocks of each wood type at each treating concentration were exhumed at each sampling interval.

Pine blocks were buried separately from the lime and beech due to the use of a higher soil moisture content for the softwood.

42 plastic boxes (265 mm long x 200 mm wide x 100 mm deep) were numbered, weighed and filled to a depth of 40 mm with soil. Blocks, grouped according to sampling interval, were selected randomly and placed with radial faces in the horizontal plane 35 mm apart on the soil surface. 20 blocks were placed in each box. Blocks to be sampled at different sampling intervals were placed in separate boxes. Block positions were noted on paper templates and a further 40 mm of soil was then placed in each box, covering the blocks. The boxes were then re-weighed to determine the weight of soil and blocks and the volume of water required to raise the soil moisture content to 80% WHC for lime and beech and 100% WHC for pine was then added. The boxes were covered with loose-fitting lids and incubated at 25°C in a thermostatically controlled dark room. Boxes were weighed weekly to check the soil moisture contents and distilled water was added as necessary to maintain the correct moisture levels.

At each sampling interval, blocks were located using the paper templates, exhumed using forceps, carefully brushed free of adhering soil and weighed immediately. They were then oven dried for 3 hours at 102°C. Moisture contents (calculated on post burial dry weight) and weight losses were then calculated for each wood block.

The dried blocks were then stored in compartmented plastic repli-plates prior to analysis.

2.2.7 Chemical analysis of wood blocks

All exhumed wood blocks and unburied control blocks were analysed individually for % $\frac{w}{w}$ nitrogen content by means of a micro-Kjeldahl technique and the residual solution subsequently analysed for % $\frac{w}{w}$ copper, chromium and arsenic contents using an atomic absorption spectrophotometer. Grade A glassware, distilled water and Analar grade reagents were used throughout.

2.2.7.1 Digestion of wood blocks

Blocks were cut longitudinally into small splinters using a sharp scalpel. Each total chopped block was transferred to a separate Kjeldahl flask and 2 cm^3 of nitrogen free concentrated H_2SO_4 was added. The flasks were transferred to a heating rack. 2 cm^3 of 100 volume H_2O_2 was added dropwise to each flask, allowing time for

the reaction to subside between the addition of each drop. The flask contents were boiled until the first signs of dense white fumes (SO_3) appeared, at which point the flasks were allowed to cool for at least two minutes prior to the addition of a further 1 cm^3 of 100 volume H_2O_2 to each flask. Heat was again applied until white fumes reappeared. Similarly, further additions of 100 volume H_2O_2 (1 cm^3 aliquots) and heating was continued until the wood blocks had completely dissolved and the solutions remained clear and free from any brown/grey colouration when the white fumes formed. Once this condition was achieved, normally after about one hour, a further 2 cm^3 of hydrogen peroxide was added to each flask and their contents were boiled for approximately two minutes to drive off excess oxygen from the samples which were then allowed to cool.

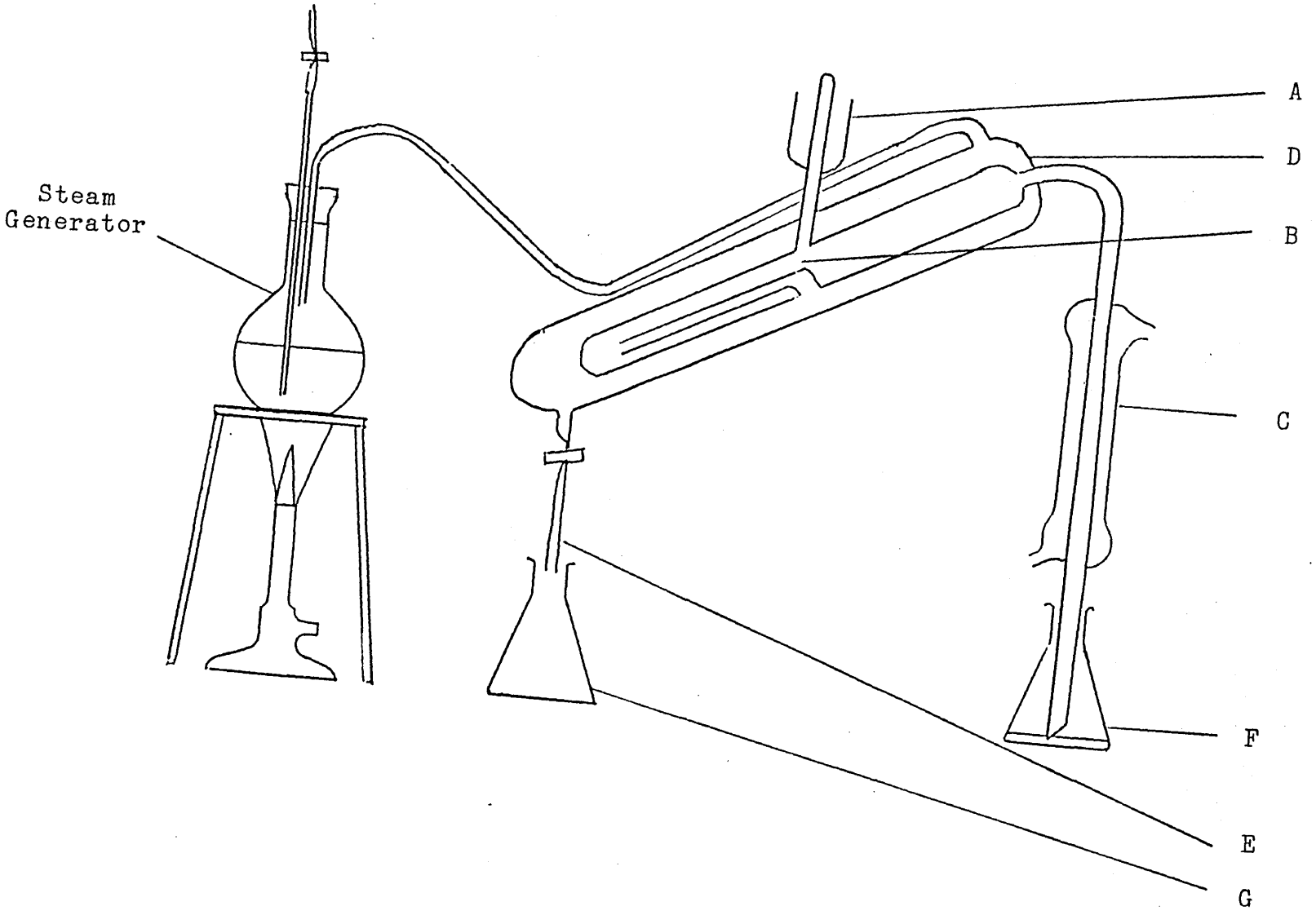
2.2.7.2 Nitrogen determination

The digest solutions were then analysed for nitrogen as ammonia using a Markham still (Fig 2.1). Nitrogen converted to ammonia during the digestion was released by the addition of excess sodium hydroxide

$$Na^+ + OH^- + NH_4^+ \longrightarrow Na^+ + H_2O + NH_{3(g)}$$

The ammonia was collected in 2% $\frac{w}{v}$ boric acid solution containing Kjeldahl indicator (0.5 g methyl red and 0.25 g methylene blue dissolved in 500 cm^3 of ethanol). The ammonia collected was titrated with standard 0.01M HCl.

Fig 2.1 Markham distillation apparatus



Procedure

Steam was passed in through the outer jacket (D) then into the inner jacket (B) and out through the condenser (C). The apparatus was steamed for ten minutes prior to each set of analyses to remove any residues from previous analyses. Care was also taken to ensure that steam was passing through the apparatus prior to the addition of each sample.

Digest samples were carefully added to funnel A and the flask rinsed twice with distilled water. The sample was then run into the inner jacket of the distillation unit (B) and the funnel rinsed twice into the unit. A 100 cm^3 conical flask (F) containing 5 cm^3 of 2% $\frac{W}{V}$ Boric acid solution and 5 drops of Kjeldahl indicator was then placed under the condenser (C). 10 cm^3 of 40% $\frac{W}{V}$ NaOH solution was then slowly added to the sample through the funnel, leaving just sufficient solution in the funnel to prevent loss of ammonia. Approximately 25 cm^3 of distillate was collected. The conical flask was then removed and the base of the condenser washed, the washings being collected in the flask. The bunsen burner was then removed from the base of the steam generator and the pressure fall created used to draw the sample from the inner to the outer jacket of the Markham still. This residual solution was then collected via tube E in a 100 cm^3 conical flask (G) containing 3 drops of Kjeldahl indicator. The unit was then rinsed twice

with distilled water added via the funnel and the washings collected in flask (G).

The green boric acid-ammonia solution was titrated against standard 0.01M HCl solution. The end point was shown by the first hint of pink colour in the flask.

The % $\frac{w}{w}$ nitrogen content of the original wood sample was calculated as follows:

$$\%N = \frac{0.014 \times \text{titre}}{\text{initial dry wt. of block}}$$

2.2.7.3 Metal analysis

The recovered digest solutions (in flask G) were re-acidified with 2.5 M H_2SO_4 solution to a pink colour. The solutions were then filtered through Whatman 541 filter paper into 100 cm^3 volumetric flasks and made up to the mark. 5 or 10 cm^3 aliquots of these solutions were then pipetted into each of three 25 cm^3 volumetric flasks, labelled A, B and C (5 cm^3 for wood blocks treated with 2.0% $\frac{w}{v}$ CCA or higher and 10 cm^3 for untreated blocks and blocks treated with less than 2.0% $\frac{w}{v}$ CCA). 1 and 2 cm^3 aliquots of a standard solution containing 25 $\mu g/cm^3$ copper and chromium and 250 $\mu g/cm^3$ arsenic were added to flasks labelled B and C respectively. All of the 25 cm^3 volumetric flasks were then made up to the mark and their contents mixed thoroughly.

The sample solutions were analysed for copper, chromium and arsenic on a Perkin Elmer 372 atomic absorption spectrophotometer by a standard additions technique.

The operating conditions for the analysis of the three elements are shown in Table 2.2.

Table 2.2

Operating conditions for the analysis of copper, chromium and arsenic by atomic absorption spectrophotometer

Element	Wavelength (nm)	Fuel	Oxidant	Flame Type	Reading Interval (seconds)
Cu	324.8	Acetylene	Air	Oxidising Lean Blue	3
Cr	357.9	Acetylene	Air	Reducing Yellow	5
As	193.7	Hydrogen	Argon	Colourless	10

Cu, Cr and As hollow cathode lamps were used for the analysis of the three elements.

The sensitivity of the spectrophotometer for each element was maximised using a machine standard solution. Separate standards were made up for each element containing 5 $\mu g/cm^3$ of copper, 2 $\mu g/cm^3$ of chromium and 40 $\mu g/cm^3$ of arsenic. The absorbance readings for these standards during analysis were at least 0.250, 0.100 and 0.400 for copper, chromium and arsenic respectively.

A.A.S. procedure

The spectrophotometer was zeroed using distilled water and checked for response for the element being analysed using the machine standard. The absorbance reading for each sample was then taken using flasks A, B and C in succession. The reading noted for each flask was an average of at least three consecutive digital readings. The spectrophotometer was then checked again for a zero reading with water. After every fourth sample, the sensitivity of the spectrophotometer was checked using the machine standard.

The concentrations of copper and chromium in the original diluted samples in the 25 cm^3 volumetric flasks without standard (flask A) were calculated as follows:

$$\mu g/cm^3 \text{ of copper or chromium} = \frac{S}{\frac{(S_1 - S) + (S_2 - S)}{3}}$$

Where S = absorbance reading for flask A (without standard)

S_1 = absorbance reading for flask B (including 1 cm^3 of standard solution)

S_2 = absorbance reading for flask C (including 2 cm^3 of standard solution)

The concentration of arsenic was calculated as above except that the value obtained was divided by ten to give the actual concentration of arsenic.

The concentrations of copper, chromium and arsenic in the 25 cm^3 volumetric flasks were then used to calculate the total µg of these elements in the original undiluted wood digests and the $\% \frac{w}{w}$ of the elements in the original wood blocks were then calculated.

2.3 Results

Mean values and standard deviations for all analyses are presented in Appendix 1.

2.3.1 Weight loss and Nitrogen content

Figures 2.2, 2.3 and 2.4 show graphs of the mean percentage weight losses and nitrogen contents of lime, beech and pine respectively during the burial period. The curves for the RSN and centre wood blocks highlight clear differences in both weight loss and nitrogen content between the two types of block for both the hardwood lime and the softwood pine.

Weight Loss

The mean weight losses for all wood types decreased with increasing CCA treating concentration and the rate of decay (shown by the slope of the curves) was apparently lower at higher preservative concentrations. The presence of CCA also produced a delay in the onset of decay: the length of the delay, or "induction phase" (Smith, *op cit*) increased with increasing treating concentration.

Lime and pine RSN blocks treated with higher concentrations of CCA showed an initial weight loss of about 10% and 5% respectively at the earliest sampling interval, followed by negligible increases in weight loss at the next sampling interval. These initial weight

losses were probably due to loss of soluble nutrients from the wood rather than decay.

In untreated lime, wood blocks containing surface nutrients showed higher percentage weight losses than centre wood blocks during the early part of the burial (Fig 2.2), but beyond 6 weeks there were no significant differences in weight loss between the RSN and centre wood. In untreated pine (Fig 2.4), percentage weight losses were higher in RSN blocks than in centre blocks at all sampling intervals, although the curves for the two types of blocks were converging at the 18 weeks sampling interval.

In CCA treated wood blocks, decay (as measured by percentage weight loss) was invariably further advanced, at any sampling interval, in blocks containing surface nutrients than in centre wood blocks treated with the same concentration of CCA. The presence of surface nutrients also reduced the length of the lag phase prior to the onset of decay, this effect being particularly marked in lime blocks treated with 1.0% $\frac{W}{V}$ CCA (Fig 2.2). At this treating concentration percentage weight loss of RSN blocks had reached almost 15% after only three weeks of soil burial whereas centre wood blocks did not show significant decay untilthe twelve weeks sampling interval.

The toxic thresholds of CCA in both lime and pine were increased by the presence of surface nutrients. The

toxic thresholds over the 18 week burial period were 2% $\frac{W}{V}$ CCA for lime centre and over 3% $\frac{W}{V}$ for lime RSN (Fig 2.2) and 0.5% $\frac{W}{V}$ CCA for pine centre and 1.0% $\frac{W}{V}$ for pine RSN (Fig 2.4).

The toxic threshold of CCA in beech without soluble nutrients was over 3.0% $\frac{W}{V}$ (Fig 2.3) and the decay patterns and rates were similar to those for lime RSN.

Both the decay rates and toxic thresholds were significantly lower for the softwood pine (Fig 2.4) than for the hardwoods.

Although blocks were not examined microscopically, examination of decayed blocks showed considerable darkening and softening of the block surfaces, features which are characteristic of soft-rot attack. Since it has also been shown that CCA inhibits growth of Basidiomycete fungi in both hardwoods and softwoods in soil (Clubbe and Levy, 1982), it was considered that the predominant decay type in CCA treated wood in this experiment was soft-rot decay.

Nitrogen content

Nitrogen contents are expressed as a % $\frac{W}{W}$ of the pre-burial dry mass of the wood blocks. Therefore, increases in the nitrogen content of blocks during decay are as a result of real inputs of nitrogen to the wood rather than an artefact caused by weight loss.

Blocks of all wood types at all CCA treating concentrations showed an increase in nitrogen content during burial in soil (Fig 2.2, 2.3 and 2.4). These nitrogen accumulations in blocks occurred both before and during decay. Wood blocks which showed weight loss at the earliest sampling intervals showed immediate increases in nitrogen content which were sustained throughout the burial period. CCA treated wood blocks in which decay commenced at later sampling intervals showed considerable increases in nitrogen content prior to the onset of decay. These increases in nitrogen content also continued after decay had commenced. Even wood blocks which showed no weight loss during the 18 week burial period showed significant increases in nitrogen content during the early part of the burial.

The nitrogen contents of some highly decayed blocks appeared to fall during the last 6 weeks of the burial. This was probably due to the fact that these blocks were so heavily decayed that they were breaking up, leading to fragments of the blocks being lost in the soil on exhumation.

Nitrogen contents were generally higher, at any sampling interval, in blocks containing surface nutrients than in centre wood blocks treated with the same concentration of CCA. These differences in nitrogen content between RSN and centre blocks were less clear in

untreated lime and pine where differences in percentage weight loss were also less marked. All CCA treated and untreated lime RSN blocks (Fig 2.2) showed continued increases in nitrogen content throughout the burial period. A similar pattern of continued increase in nitrogen content also occurred in lime centre blocks except those treated with 1.5 and 2.0% $\frac{w}{v}$ CCA. These blocks, which did not undergo heavy decay during the burial, only showed significant increases in nitrogen content during the first six weeks of soil burial.

In CCA treated lime, the rate of increase in nitrogen content (as determined by the slope of the curves) appeared to be greater in RSN blocks than in centre blocks treated with the same concentration of CCA.

In pine blocks (Fig 2.4), the effect of surface nutrients on the nitrogen dynamics during soil burial was less clear. Although RSN blocks had a higher nitrogen content, at any sampling interval, than centre wood blocks, there was no obvious difference in the rate of increase in nitrogen content between RSN and centre blocks treated with the same CCA concentration. All pine RSN and centre blocks showed increases in nitrogen content during the first six weeks of soil burial. However, these nitrogen increases only continued in blocks which subsequently decayed.

Although the presence of CCA both increased the length of the lag phase prior to decay and reduced the rate of decay, the presence of this preservative only slightly depressed the rate of increase in nitrogen content, as compared to untreated blocks, except in those blocks which showed no significant weight loss during the burial period.

2.3.2 Statistical treatment of weight loss and nitrogen data

Both percentage weight loss and nitrogen data were analysed individually using a two-way analysis of variance. A linear correlation of weight loss against nitrogen content was also performed for all wood types and treatments.

The statistical analysis was carried out using the "Statpack" programme (R. Houchard, Western Michigan University, 1974) on a Decsystem 20 computer.

Tables 2.3 and 2.4 show the probability values obtained using the two-way analyses of variance to compare the weight loss and nitrogen data respectively for surface and centre wood pine and lime blocks at each preservative treatment level.

In Table 2.3 the column headed "Centre/surface" shows that differences in weight loss between the surface and centre wood blocks of each species at all preservative treatment levels were highly significant. The "Interaction"

column shows that highly significant differences in rates of decay existed between centre and surface blocks of both wood types at all CCA treating concentrations where decay occurred. The presence of concentrations of soluble nutrients in the RSN blocks clearly decreased the effectiveness of the CCA preservative and stimulated microbial decay of the treated wood.

In Table 2.4, the column headed "Centre/surface" shows that differences in nitrogen content between the surface and centre wood blocks of both lime and pine at all preservative treatment levels were highly significant. The "Interaction" column shows highly significant differences in rates of nitrogen input between surface and centre wood blocks of both wood types at all CCA treating concentrations and in untreated pine. Thus, the presence of surface nutrients produced higher nitrogen contents and stimulated nitrogen inputs in CCA treated RSN blocks.

Table 2.5 shows correlation coefficients of weight loss and nitrogen contents for all wood types and treating concentrations over the burial period. In most cases, weight loss was not highly correlated with nitrogen content. However, in pine centre and RSN blocks and in lime centre blocks, weight loss and nitrogen content were more strongly correlated at lower CCA treating concentrations and particularly in untreated wood. This trend was not apparent in beech blocks or in lime RSN blocks. In lime

RSN blocks the trend was apparently reversed, with the highest coefficients at the highest CCA treating concentrations.

2.3.3 Preservative data

Figs 2.5, 2.6 and 2.7 show the mean percentage copper and chromium contents of lime, beech and pine respectively during the burial. Similar graphs of their arsenic contents are shown in Figs 2.8, 2.9 and 2.10.

The mean values of copper, chromium and arsenic contents for lime and pine unburied control blocks (Figs 2.5, 2.7, 2.8, 2.10) show that RSN blocks contained lower concentrations of all three toxic elements than centre wood blocks treated with the same concentration of CCA.

There was generally an apparent fall in copper, chromium and arsenic contents in blocks during soil burial, suggesting that preservative elements were lost from the wood blocks into the surrounding soil.

Percentage losses of copper, chromium and arsenic were calculated for all wood types at all CCA treating concentrations using the mean values of preservative analysis of unburied control blocks and blocks from the 18 week sampling interval. These percentage losses are shown in Table 2.6.

Percentage losses of all three toxic elements were generally higher at lower CCA treatment levels in all wood types and lime centre treated with 2.0% $\frac{W}{V}$ CCA and beech treated with 3% $\frac{W}{V}$ CCA showed negligible losses of copper and chromium.

The mean values for the preservative analyses (Figs 2.5 to 2.10) and the percentage losses calculated (Table 2.6) suggest that lime and pine blocks containing surface nutrients lost more copper, chromium and arsenic during soil burial than centre wood blocks treated with the same concentration of CCA. For pine and lime data taken together, the surface blocks on average lost 14% more copper and 20% more chromium and arsenic than the centre blocks.

Most losses of preservative elements occurred during the first three to six weeks of burial in soil, although some heavily decayed blocks also showed small losses during the last six weeks of soil burial. After initial preservative losses, most blocks showed no further significant losses despite considerable weight loss in many cases. Thus, as the amount of wood substance fell during decay, the effective concentration of preservative in the remaining wood increased.

Copper, chromium and arsenic concentrations in unburied control blocks calculated from liquid uptake data (Appendix I) were compared with concentrations

determined by chemical analysis. Ratios of analytical concentrations to concentration calculated from liquid uptake data are presented in Table 2.7. Each wood species showed typical adsorption behaviour towards the three preservative elements during impregnation. The highest ratios of analysed to uptake element concentrations were found at the lowest treating concentrations.

2.3.4 Statistical treatment of preservative data

The analytically determined copper, chromium and arsenic concentrations were analysed statistically using one-way and two-way analyses of variance and t-tests.

Table 2.8 shows the probability values obtained using one and two-way analyses of variance to compare preservative element concentrations of surface and centre wood pine and lime blocks during soil burial. Each preservative treatment level was analysed individually. The "Centre" and "Surface" columns show the results of one-way analyses of variance testing for significant changes in preservative element concentrations during soil burial. The centre and surface columns for copper show that, with the exception of lime centre treated with 2.0% $\frac{w}{v}$ CCA, all centre and surface blocks of both lime and pine showed highly significant losses of copper. The centre and surface columns for chromium and arsenic also show significant losses of these elements in most cases. The "Interaction" columns show the results of

two-way analyses of variance testing for significant effects of surface nutrients on the rate of change in preservative element concentration during burial. The results of the two-way analyses of variance show that, in most cases, surface nutrients did not significantly affect the rate of loss of copper, chromium and arsenic from wood blocks during soil burial.

Table 2.9 shows probability values obtained using t-tests to compare preservative element concentrations of centre and RSN blocks at each sampling interval for each treating concentration. The results of these tests show that there were no significant differences between unburied centre and RSN block preservative concentrations at most treatment levels. However, by the end of the burial period, significant differences were found for each element at all CCA treatment levels except for arsenic in the lime RSN blocks. The variability in the arsenic data could mask any differences due to surface nutrients.

Therefore the statistical analyses of the preservative data show that CCA treated pine and lime surface and centre blocks showed significant losses of copper, chromium and arsenic at most treatment levels and that losses of all three preservative elements were generally significantly greater from the surface blocks than the centre blocks.

Fig. 2.2 Mean % weight loss and $\%\frac{w}{w}$ nitrogen contents of untreated and CCA treated lime blocks during soil burial.

□ △ = RSN wood

■ ▲ = centre wood

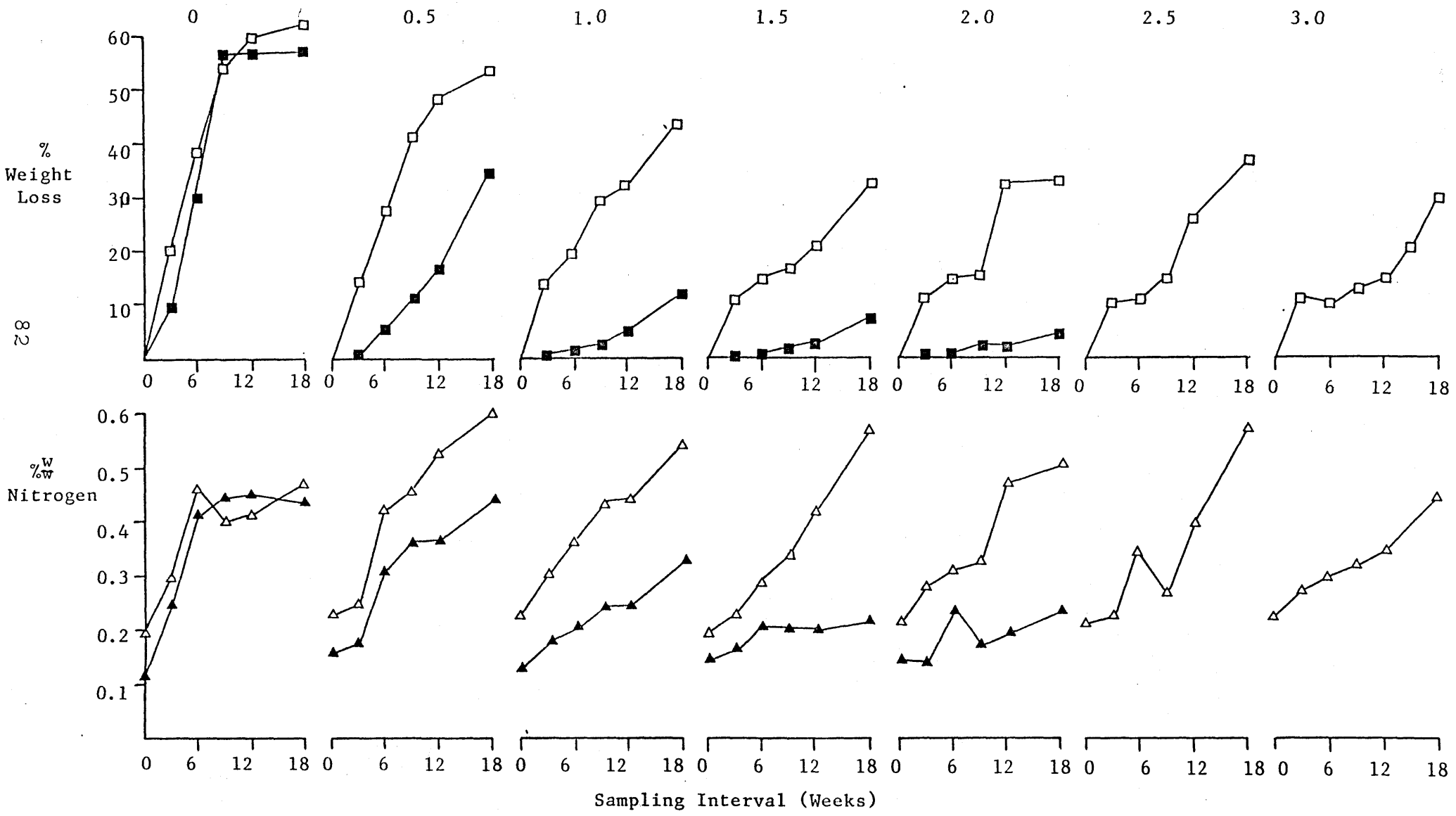

CCA TREATING CONCENTRATION (%w/v)
0
0.5
1.0
1.5
2.0
2.5
3.0
% Weight Loss
%w/w Nitrogen
Sampling Interval (Weeks)

Fig. 2.3 Mean % weight loss and $\%\frac{w}{w}$ nitrogen contents of untreated and CCA treated beech blocks during soil burial.

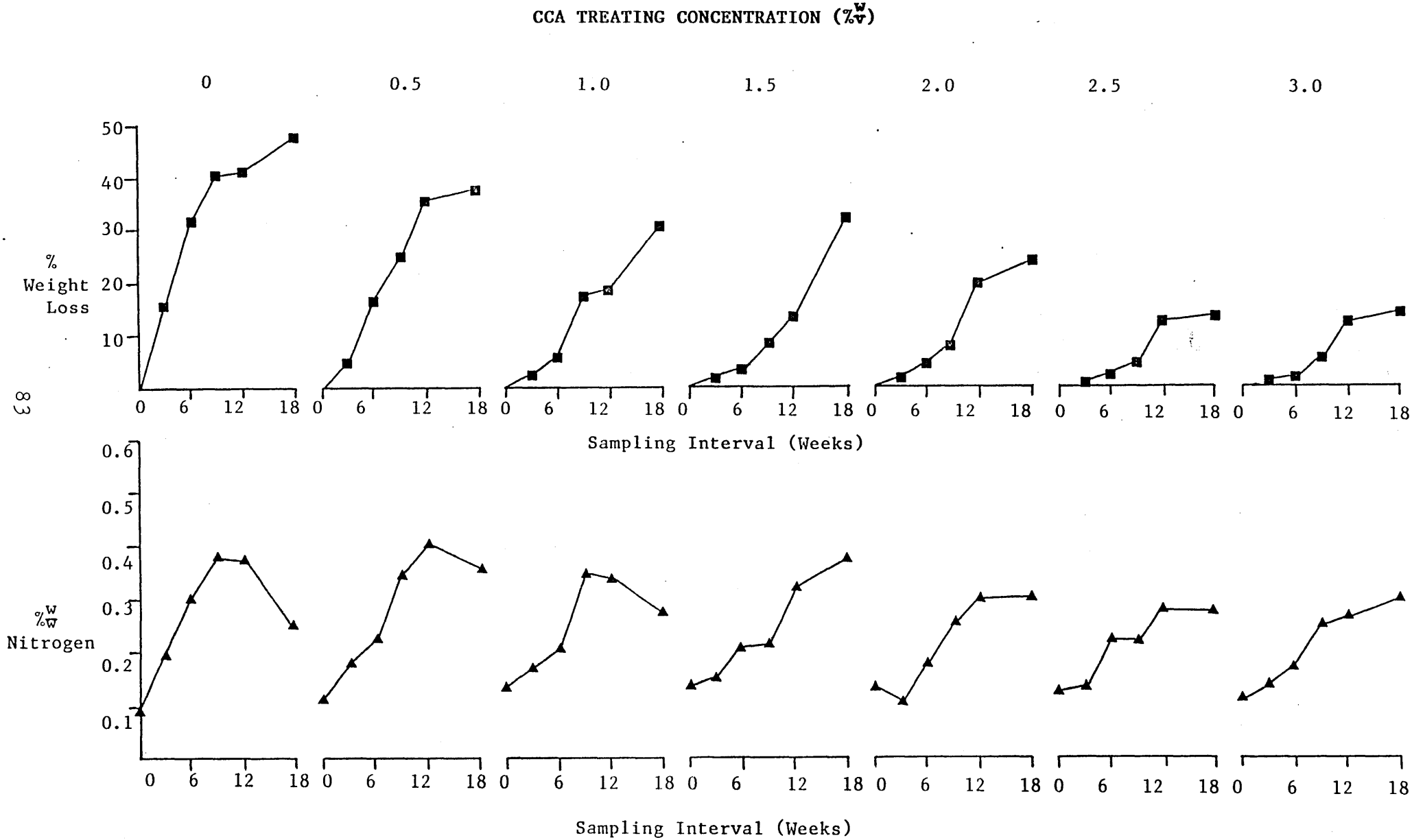

CCA TREATING CONCENTRATION (%w/w)
0
0.5
1.0
1.5
2.0
2.5
3.0
% Weight Loss
50
40
30
20
10
0
6
12
18
Sampling Interval (Weeks)
%w/w Nitrogen
0.6
0.5
0.4
0.3
0.2
0.1
Sampling Interval (Weeks)

Fig. 2.4 Mean % weight loss and $\%\frac{w}{w}$ nitrogen contents of untreated and CCA treated pine blocks during soil burial.

□ △ = RSN wood

■ ▲ = centre wood

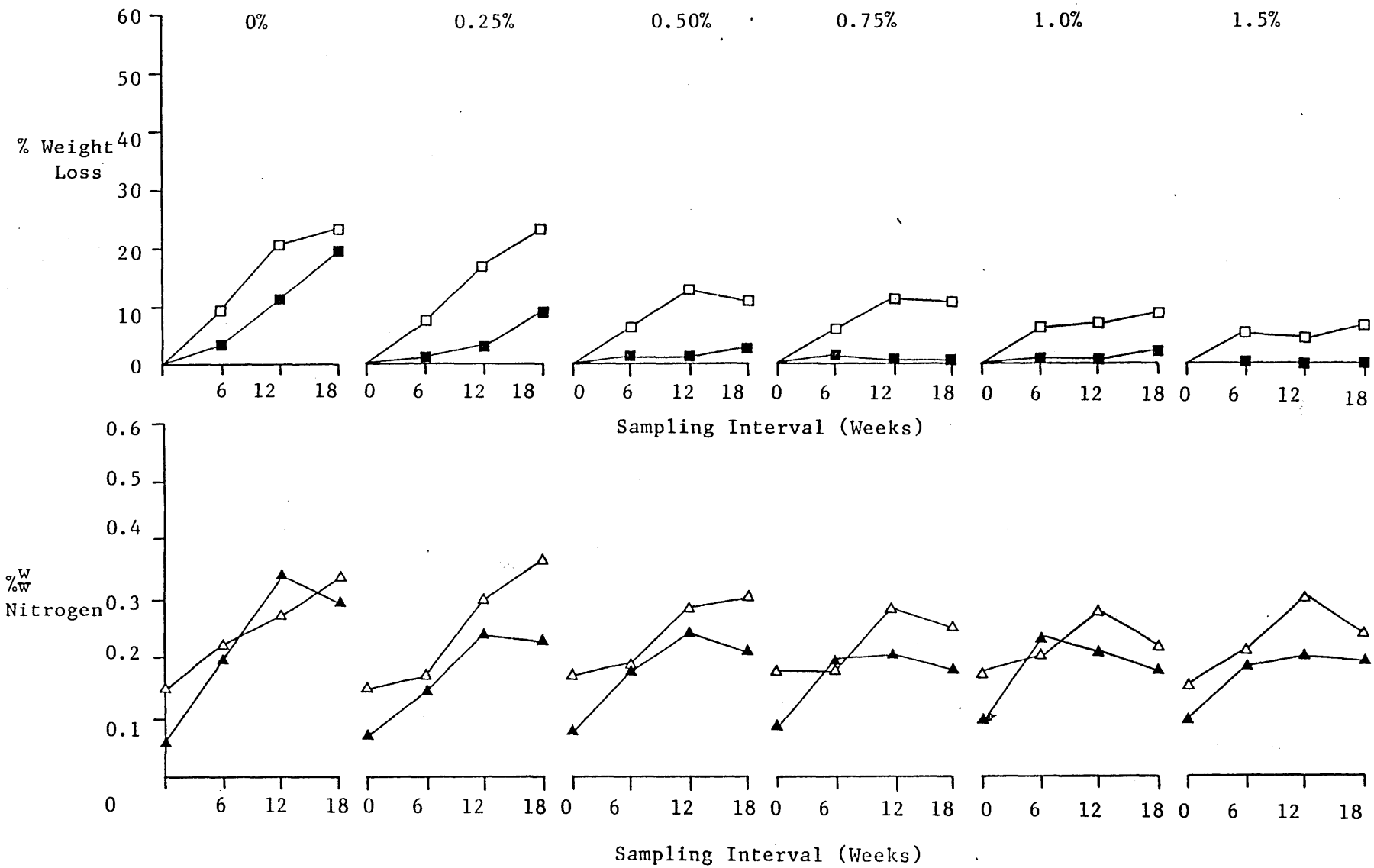

CCA TREATING CONCENTRATION (%w/w)
0%
0.25%
0.50%
0.75%
1.0%
1.5%
% Weight Loss
60
50
40
30
20
10
0
6
12
18
Sampling Interval (Weeks)
%w/w Nitrogen
0.6
0.5
0.4
0.3
0.2
0.1
0
Sampling Interval (Weeks)

Fig. 2.5 Mean $\frac{w}{w}$% copper and chromium contents of CCA treated lime blocks during soil burial.

○ = RSN wood

● = centre wood

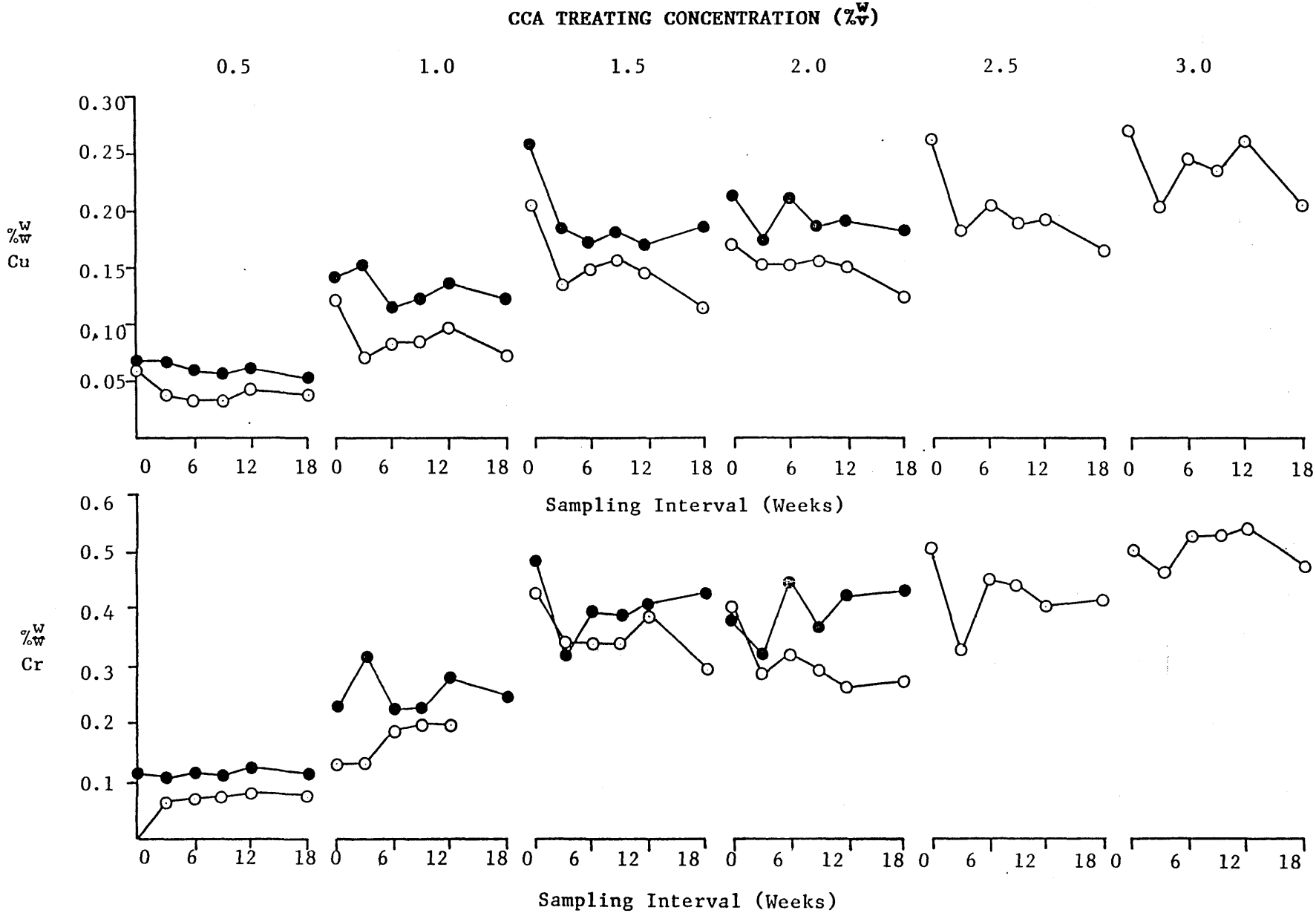

CCA TREATING CONCENTRATION (%w/v)
0.5
1.0
1.5
2.0
2.5
3.0
%w Cu
0.30
0.25
0.20
0.15
0.10
0.05
0 6 12 18
Sampling Interval (Weeks)
%w Cr
0.6
0.5
0.4
0.3
0.2
0.1
0 6 12 18
Sampling Interval (Weeks)

Fig. 2.6 Mean $\%\frac{w}{w}$ copper and chromium contents of CCA treated beech blocks during soil burial.

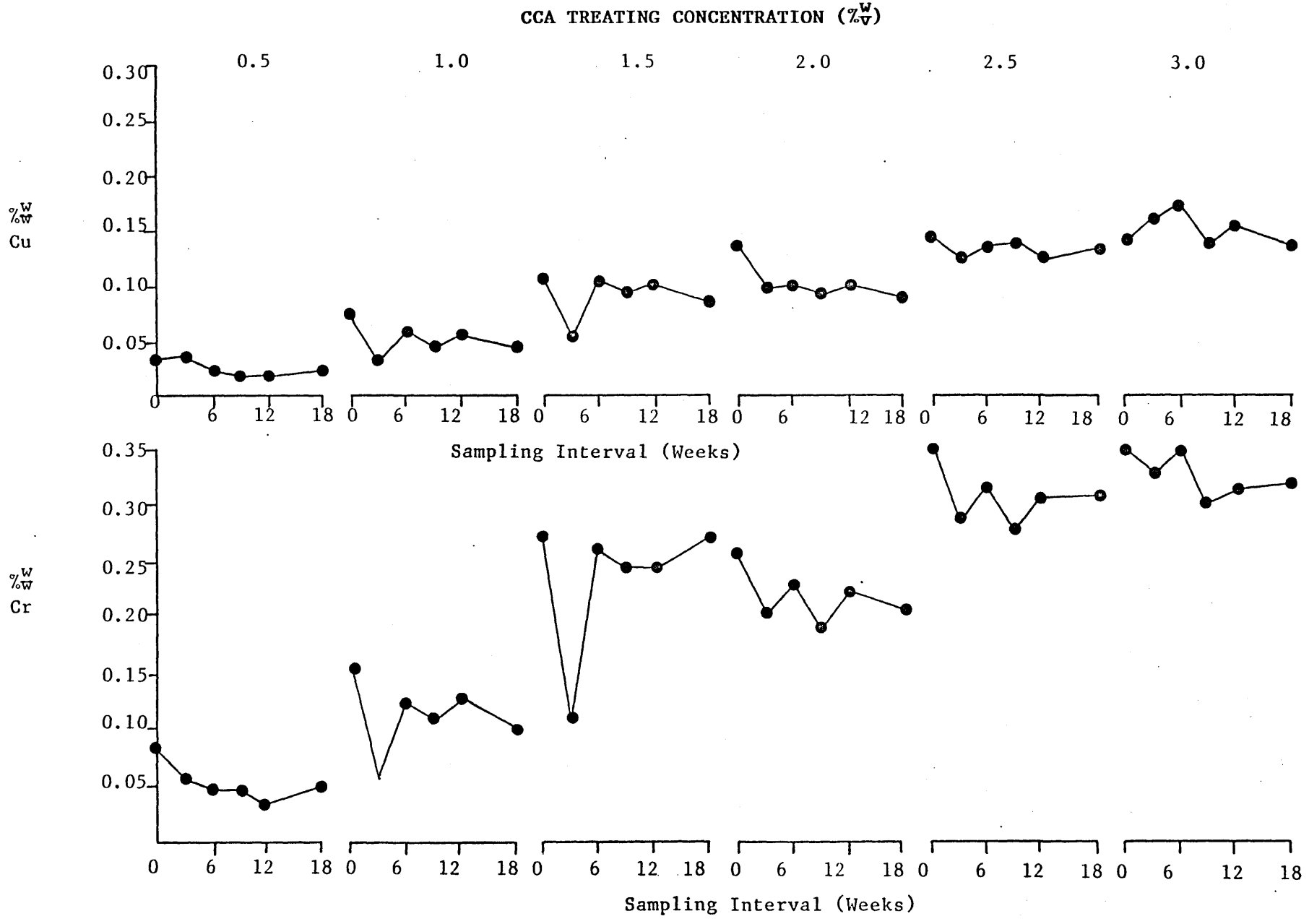

CCA TREATING CONCENTRATION (%w/v)
0.5
1.0
1.5
2.0
2.5
3.0
%w Cu
0.30
0.25
0.20
0.15
0.10
0.05
0
6
12
18
Sampling Interval (Weeks)
%w Cr
0.35
0.30
0.25
0.20
0.15
0.10
0.05
Sampling Interval (Weeks)

Fig. 2.7 Mean $\%\frac{w}{w}$ copper and chromium contents of CCA treated pine blocks during soil burial.

○ = RSN wood

● = centre wood

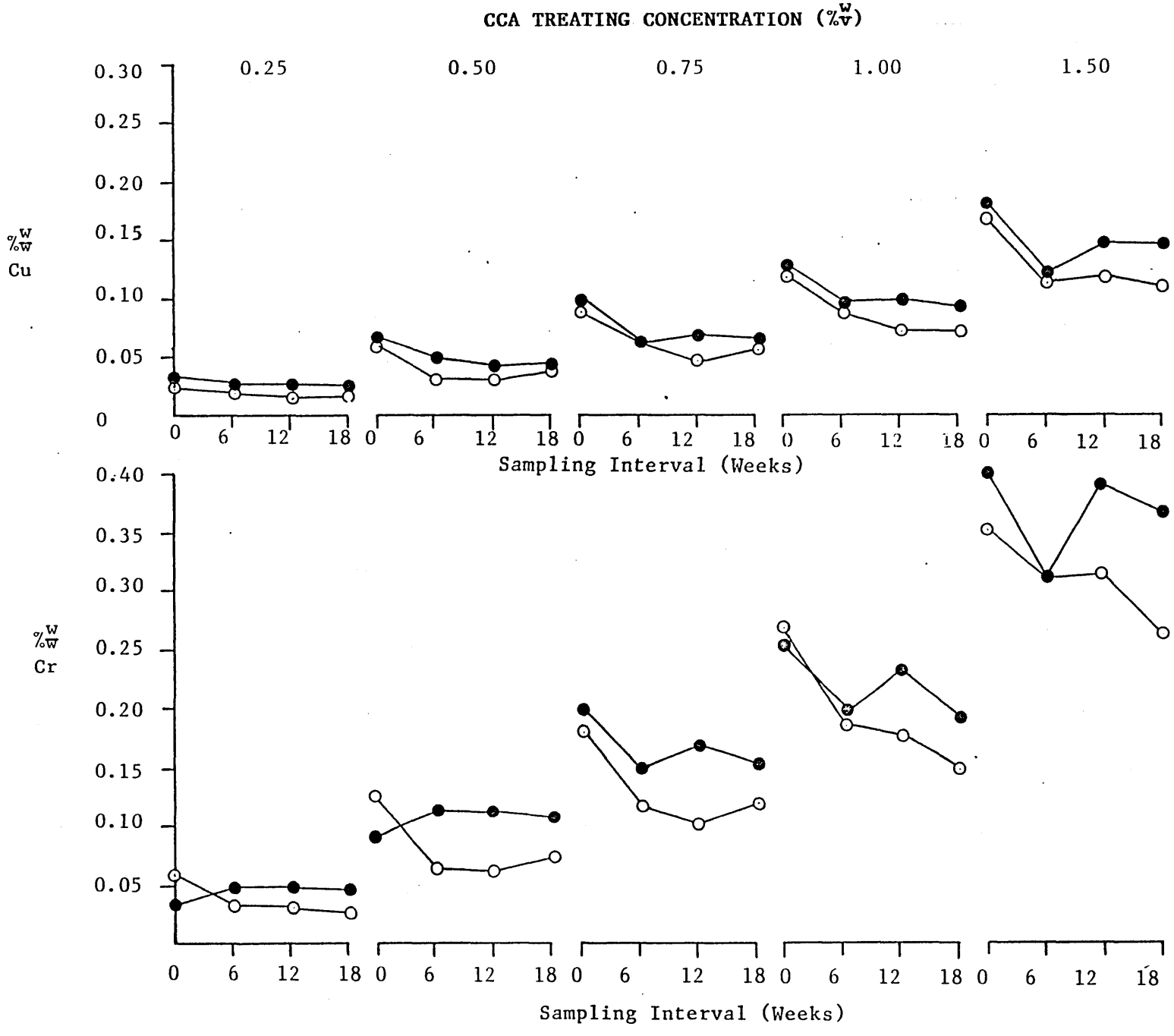

CCA TREATING CONCENTRATION (%w/v)
0.25
0.50
0.75
1.00
1.50
%w Cu
0.30
0.25
0.20
0.15
0.10
0.05
0
0 6 12 18
Sampling Interval (Weeks)
%w Cr
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0 6 12 18
Sampling Interval (Weeks)

Fig. 2.8 Mean $\%\frac{w}{w}$ arsenic contents of CCA treated lime blocks during soil burial.

● = RSN wood

⊙ = centre wood

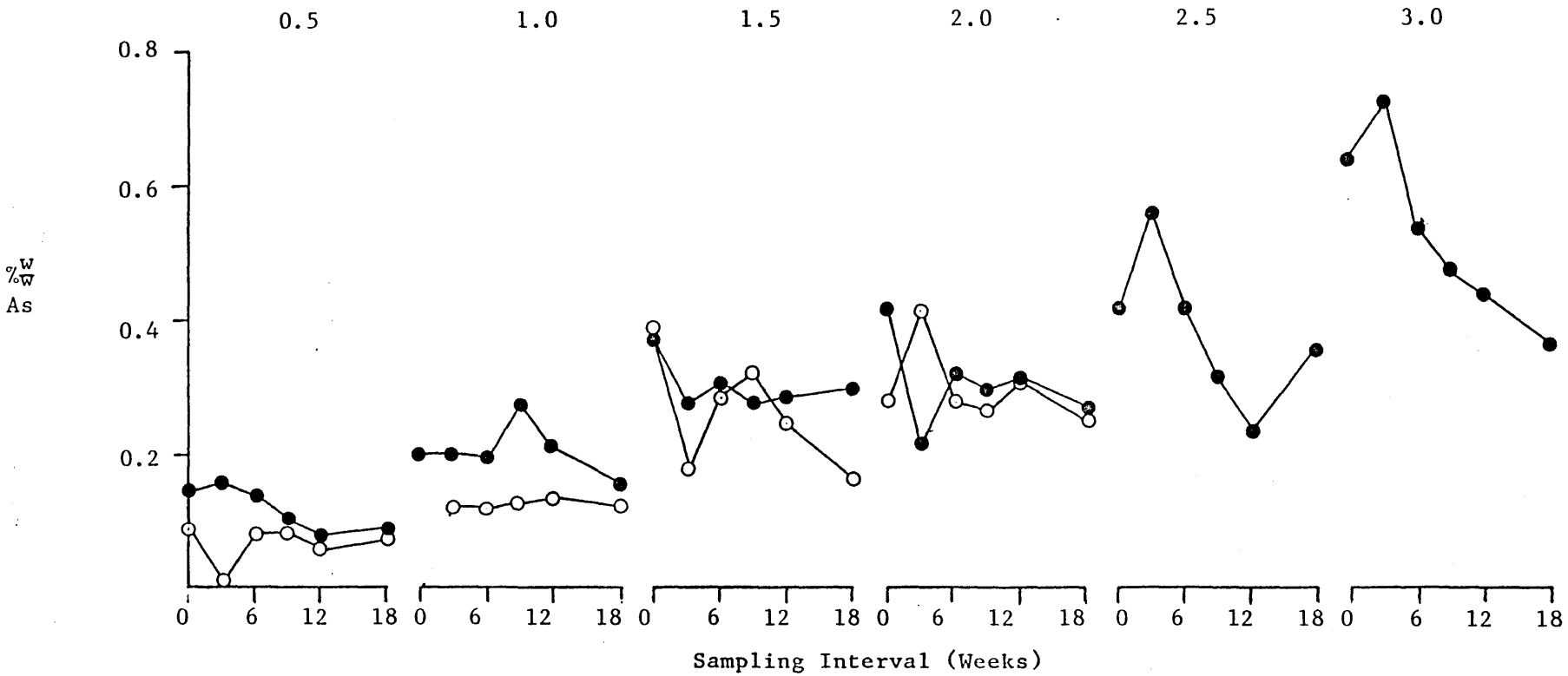

CCA TREATING CONCENTRATION (%w/v)
0.5
1.0
1.5
2.0
2.5
3.0
0.8
0.6
0.4
0.2
%w/w As
0
6
12
18
Sampling Interval (Weeks)

Fig. 2.9 Mean $\%\frac{w}{w}$ arsenic contents of CCA treated beech blocks during soil burial.

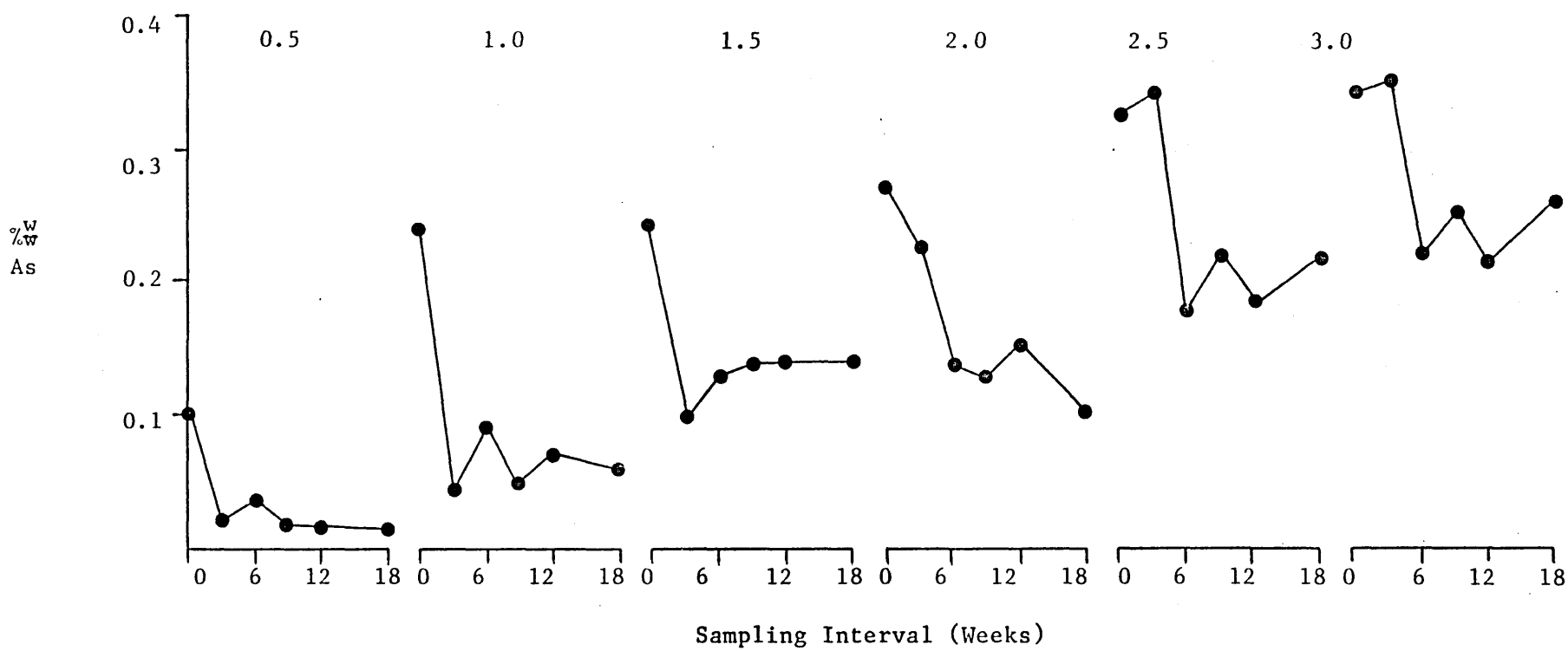

CCA TREATING CONCENTRATION (%w/v)
0.5
1.0
1.5
2.0
2.5
3.0
0.4
0.3
0.2
0.1
%w/w As
0 6 12 18
Sampling Interval (Weeks)

Fig. 2.10 Mean $\%\frac{w}{w}$ arsenic contents of CCA treated pine blocks during soil burial.

○ = RSN wood

● = centre wood

CCA TREATING CONCENTRATION (%$\frac{w}{v}$)

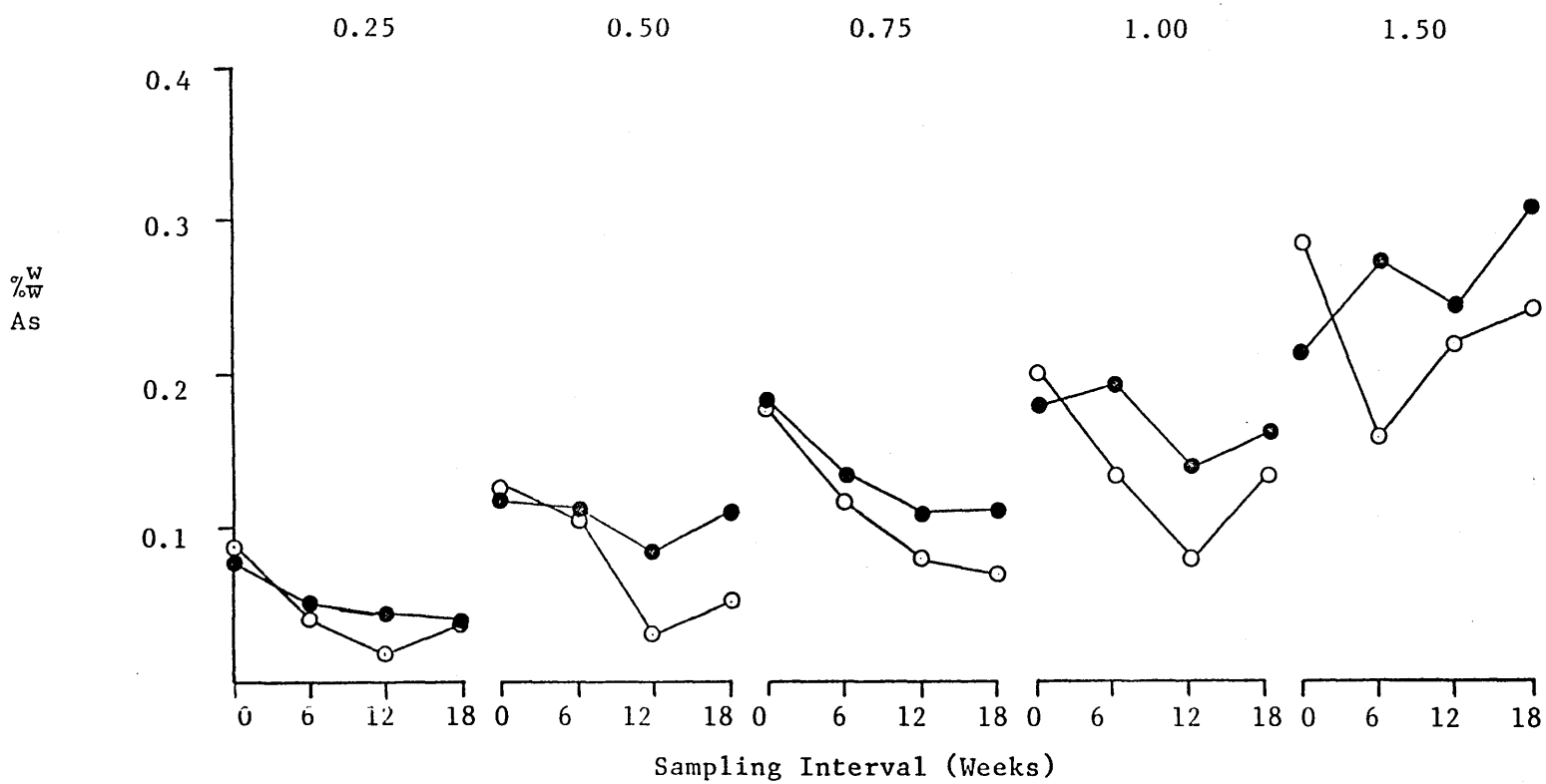


Table 2.3

2-way analysis of variance comparison of weight loss differences between buried surface and centre sapwood blocks

Wood Type	I % CCA	II Time Interval	III Centre/ Surface Woods	IV Interaction
Lime	0	XXX	X	NS
	0.5	XXX	XXX	XX
	1.0	XXX	XXX	XXX
	1.5	XXX	XXX	XXX
	2.0	XXX	XXX	XXX
Pine	0	XXX	XXX	NS
	0.25	XXX	XXX	XXX
	0.50	XXX	XXX	XX
	0.75	XX	XXX	XX
	1.00	XX	XXX	NS
	1.50	NS	XXX	NS

XXX, XX, X and NS represent probabilities of <0.1, 1.0, 5, and >5% respectively, that differences arising from the comparisons of each column could arise by chance.

Column I Treatment

Column II Shows whether there is a significant weight loss over the burial period for the combined surface and centre wood blocks.

Column III Shows for the combined time intervals whether there is a significant difference in weight loss between the centre and surface wood blocks.

Column IV Shows any significant differences between weight losses for centre and surface wood blocks from time interval to interval over the burial period.

Table 2.4

2-way analysis of variance comparison of nitrogen content of buried surface and centre blocks

Wood Type	I % CCA	II Sampling Interval	III Centre/ Surface	IV Interaction
Lime	0	XXX	NS	NS
	0.5	XXX	XXX	XXX
	1.0	XXX	XXX	XXX
	1.5	XXX	XXX	XXX
	2.0	XXX	XXX	XXX
Pine	0	XXX	NS	XXX
	0.25	XXX	XXX	XX
	0.50	XXX	XXX	XX
	0.75	XXX	XXX	XXX
	1.00	XXX	XXX	XXX
	1.50	XXX	XXX	XXX

XXX, XX, X and NS represent probabilities of <0.1, 1.0, 5, and >5% respectively, that differences arising from the comparisons of each column could arise by chance.

Column I Treatment

Column II Shows whether there is any significant change in nitrogen content over the burial period for the combined surface and centre sapwood blocks.

Column III Shows for the combined time intervals whether there is a significant difference in nitrogen content between the surface and centre sapwood blocks.

Column IV Shows any significant differences between nitrogen contents for centre and surface sapwood blocks from time interval to interval over the burial period.

Table 2.5

Correlation coefficients of % weight loss versus % $\frac{w}{w}$ nitrogen content for untreated and CCA treated lime, pine and beech blocks during soil burial

% $\frac{w}{v}$ CCA	Correlation Coefficients				
	Wood Type				
	Pine Centre	Pine RSN	Beech	Lime Centre	Lime RSN
0	0.7737	0.8827	0.7632	0.7651	0.6697
0.25	0.6092	0.9330	-	-	-
0.50	0.4576	0.8418	0.8134	0.6059	0.7790
0.75	0.4747	0.7808	-	-	-
1.00	0.0645	0.5425	0.6678	0.6394	0.8979
1.50	0.3608	0.6295	0.8352	0.4472	0.6775
2.00	-	-	0.7692	0.4306	0.9484
2.50	-	-	0.7440	-	0.8650
3.00	-	-	0.8448	-	0.9073

Table 2.6

Percentage loss of copper, chromium and arsenic from CCA treated wood blocks during soil burial

Wood Type	CCA Treating Concentration % $\frac{w}{v}$	Percentage Loss		
		Copper	Chromium	Arsenic
Pine Centre	0.25	20.6	8.8	49.4
	0.50	26.7	0	6.0
	0.75	23.8	15.6	12.4
	1.00	21.7	20.8	3.0
	1.50	21.1	16.1	0
Pine RSN	0.25	40.0	53.7	55.2
	0.50	35.7	38.6	57.5
	0.75	31.6	27.4	58.3
	1.00	32.4	38.5	26.5
	1.50	31.2	21.5	14.2
Beech	0.5	38.5	35.0	75.0
	1.0	24.6	17.1	68.3
	1.5	21.1	2.5	42.3
	2.0	23.7	10.8	57.1
	2.5	7.6	13.7	33.2
	3.0	0	5.3	20.4
Lime Centre	0.5	18.5	0	38.3
	1.0	14.8	0	42.1
	1.5	20.9	2.3	20.2
	2.0	0	0	32.7
Lime RSN	0.5	47.8	46.7	44.4
	1.0	29.6	-	36.1
	1.5	18.8	37.9	37.9
	2.0	36.2	34.7	34.7
	2.5	28.8	15.6	15.6
	3.0	16.7	27.7	27.7

Table 2.7

Selective absorption ratios of copper, chromium and arsenic for CCA treated pine, beech and lime blocks

Wood Type	% $\frac{w}{v}$ CCA	Selective Absorption Ratios		
		Copper	Chromium	Arsenic
Pine Centre	0.25	1.36	0.78	2.55
	0.50	1.11	0.85	1.70
	0.75	1.38	1.66	2.21
	1.00	1.21	1.36	1.37
	1.50	1.19	1.52	1.17
Pine RSN	0.25	1.36	1.38	3.22
	0.50	1.07	1.19	1.79
	0.75	1.12	1.34	1.85
	1.00	1.07	1.42	1.51
	1.50	1.06	1.23	1.44
Beech	0.5	1.30	1.60	2.78
	1.0	1.11	1.26	2.74
	1.5	0.96	1.36	1.73
	2.0	1.04	1.14	1.69
	2.5	0.84	1.17	1.54
	3.0	0.74	1.02	1.42
Lime Centre	0.5	1.22	1.16	1.96
	1.0	1.21	1.10	1.36
	1.5	1.18	1.25	1.37
	2.0	0.89	1.10	1.73
Lime RSN	0.5	1.37	1.52	1.61
	1.0	-	-	-
	1.5	1.06	1.24	1.63
	2.0	1.03	1.12	1.09
	2.5	0.95	1.04	1.24
	3.0	0.84	0.90	1.63

Table 2.8

One and two way analyses of variance on wood block copper, chromium and arsenic contents, to detect significance of losses occurring during soil burial and possible effect of surface nutrients on rates of loss

Wood Type	% $\frac{w}{CCA}$	Copper			Chromium			Arsenic		
		Centre	Surface	Inter-action	Centre	Surface	Inter-action	Centre	Surface	Inter-action
Lime	0.5	NS	XXX	NS	NS	XXX	NS	XX	XXX	NS
	1.0	XX	XXX	NS	XX	NT	NS	XXX	NT	NS
	1.5	XXX	XXX	NS	X	XXX	NS	XX	XXX	NS
	2.0	NS	XXX	XXX	NS	XXX	NS	XX	XXX	NS
	2.5	NT	XXX	NT	NT	NS	NT	NT	XXX	NT
	3.0	NT	X	NT	NT	NS	NT	NT	XXX	NT
Pine	0.25	XXX	XXX	NS	NS	XXX	X	NS	X	NS
	0.50	XXX	XXX	X	X	XXX	XXX	NS	XXX	NS
	0.75	XXX	XXX	NS	X	XX	NS	X	XXX	NS
	1.00	X	XXX	X	X	XXX	NS	NS	XXX	XXX
	1.50	XXX	XXX	NS	XX	NS	NS	XXX	NS	XXX

XXX, XX, X and NS represent probabilities of <0.1, 1.0, 5 and <5% respectively, that differences arising from the comparisons of each column could arise by chance. NT indicates no trial.

The "centre" and "surface" columns show results for one-way ANOVAs testing for significant changes in Cu, Cr and As concentration during burial time.

The interaction column shows results for two-way ANOVA's testing for significant effects of surface nutrients on the rate of change of Cu, Cr and As concentration during burial.

Table 2.9

'T-Test' comparisons of copper, chromium and arsenic retentions of surface and centre blocks prior to and after soil burial

Wood Type	% CCA	Toxic Element	Sampling Interval (Weeks)					
			0	3	6	9	12	18
Lime	0.5	Cu	X	NS	XXX	XXX	XX	XX
	1.0	"	X	XXX	XX	X	XXX	XX
	1.5	"	NS	XX	NS	X	NS	XXX
	2.0	"	NS	NS	XX	X	XX	XX
Lime	0.5	Cr	NS	NS	X	XX	XXX	XX
	1.0	"	XXX	XXX	NS	XXX	XXX	NT
	1.5	"	NS	NS	NS	X	XXX	XXX
	2.0	"	NS	NS	X	NS	XX	XX
Lime	0.5	As	NS	XXX	NS	XXX	XX	NS
	1.0	"	NS	X	NS	XXX	XX	NS
	1.5	"	NS	NS	NS	NS	NS	NS
	2.0	"	X	X	NS	SS	NS	NS
Pine	0.25	Cu	X	NT	XXX	NT	XXX	XX
	0.50	"	X	NT	XXX	NT	XXX	X
	0.75	"	NS	NT	XX	NT	XXX	NS
	1.00	"	NS	NT	NS	NT	XXX	XX
	1.50	"	NS	NT	NS	NT	X	XXX
Pine	0.25	Cr	NS	NT	XX	NT	X	XX
	0.50	"	NS	NT	XXX	NT	XXX	XXX
	0.75	"	NS	NT	NS	NT	XXX	X
	1.00	"	NS	NT	NS	NT	XXX	XXX
	1.50	"	S	NT	NT	NT	NS	XXX
Pine	0.25	As	NS	NT	NS	NT	X	XX
	0.50	"	NS	NT	NS	NT	XXX	X
	0.75	"	NS	NT	NS	NT	NS	XX
	1.00	"	NS	NT	NS	NT	XX	XXX
	1.50	"	X	NT	NT	NT	NS	X

Probabilities of differences between Cu, Cr and As concentrations of surface and centre blocks being due to chance alone -

X = P < 5% XX = P < 1.0% XXX = P < 0.1%

NS = No significant difference NT = No trial

2.4 Discussion

In terms of the main aims of this experiment, the following conclusions can be drawn:

1. Surface nutrients increased the toxic thresholds of CCA in both lime and pine (Figs 2.2 and 2.4) and increased the rate of decay at any CCA treating concentration (Table 2.3).

2. Surface nutrients increased the rate of nitrogen input to CCA treated wood (Table 2.4) and thus stimulated the microbial invasion of this wood.

3. Significant losses of preservative elements did occur from pine and lime blocks at most CCA treatment levels (Table 2.8). These losses occurred mostly during the first three to six weeks of soil burial (Figs 2.5 - 2.10). After these initial losses, there was an effective increase in the concentration of preservative in the remaining wood substance during decay, caused by loss of wood mass. Preservative losses, on a percentage basis, decreased with increasing CCA treatment level (Table 2.6).

4. Surface nutrients increased the losses of preservative elements from CCA treated lime and pine during soil burial (Tables 2.6 and 2.9).

5. Copper, chromium and arsenic were absorbed selectively by wood from CCA treating solutions during impregnation (Table 2.7). Selective absorption ratios for all three elements fell with increasing CCA treating concentration.

In addition, the following conclusions may be drawn:

1. The presence of CCA increased the length of the induction phase prior to decay (the period of time elapsing after burial in soil before significant decay occurs) (Figs 2.2 - 2.4).

2. The presence of surface nutrients in CCA treated wood decreased the length of the induction phase (Figs 2.2 and 2.4).

3. The presence of CCA depressed the rate of decay considerably but only slightly depressed the rate of nitrogen input to blocks which decayed (Figs 2.2 - 2.4).

4. Increases in nitrogen content only occurred during the early stages of burial of CCA treated wood blocks which showed no decay (Figs 2.2 and 2.4).

The nitrogen and weight loss data (Figs 2.2 - 2.4) show that increases in the nitrogen content of wood are associated with the decay of both CCA treated and untreated wood in soil.

In untreated lime RSN and centre blocks and beech blocks, both increases in nitrogen content and weight loss occurred during the first three weeks of soil burial. Nitrogen content was not strongly correlated with weight loss (coefficients were 0.76, 0.77 and 0.67 for beech, lime centre and lime RSN respectively). Although this finding contrasts with that of Waite and King (1979), their studies concentrated on the early stages of wood decay with burial periods of up to only 8 weeks. It is likely that in the later stages of decay, saturation of wood with nitrogen occurs such that decay continues without continued large increases in nitrogen content.

The association of nitrogen transfer to wood with decay during the early stages of soil burial suggests that increases in the nitrogen content of wood are caused, at least in part, by an input of microbial biomass to the wood from soil. Micro-organisms contain far more nitrogen than undecayed wood and therefore a movement of micro-organisms into wood causes an increase in wood nitrogen content. Also, since the wood blocks were completely buried in soil, it is unlikely that significant uptake of soil salts due to wick action would have occurred. Bacteria are generally the first colonisers of wood in soil (Clubbe and Levy, 1982) and their movement into wood, possibly due to chemotactic attraction (Mowe, 1984), could cause a significant increase in wood nitrogen content (King, Henderson and Murphy, 1980).

The subsequent "invasion" of wood by fungi growing actively into the wood across the wood/soil interface, possibly due to chemotropic responses of fungi to wood volatiles, as demonstrated by Mowe, King and Senn (1983) might cause a further increase in wood nitrogen content, as suggested by Waite and King (1979). This invasion of wood contrasts with colonisation of wood by micro-organisms (which might arise from spore germination at wood surfaces) in which no contact with the soil is necessary and growth of organisms is at the expense of wood nutrients. King and Waite (1980) did not find a significant correlation between the nitrogen content and weight loss of wood blocks exposed to Basidiomycete attack in pure culture studies. These fungi are frequently found in decaying wood in situations where nutrient inputs to wood are not possible and they may have the ability to re-absorb nitrogenous materials from autolysing mycelium in order to conserve nitrogen (Cowling and Merrill, 1966).

The rates of decay and increase in nitrogen content were far lower in pine than in lime and beech and increases were observed in the nitrogen content of untreated pine blocks prior to the onset of decay (Fig 2.4). These increases may represent a microbial invasion of wood, caused by a chemostimulation of the soil microflora, leading to the establishment of threshold nitrogen or microbial levels in wood above which decay can occur. The lower rate of nitrogen increase in pine blocks suggests

that the level of chemostimulation caused by this wood type is lower than in the hardwoods used. Levi and Cowling (1969) considered that a carbon : nitrogen ratio of less than 140 : 1 (equivalent to approximately 0.2% $\frac{w}{w}$ nitrogen was required before soft-rot microfungi could become actively cellulolytic. Decay was not observed in pine blocks with nitrogen contents below this figure.

Weight loss and nitrogen data for lime and pine blocks (Figs 2.2 and 2.4) suggest that surface nutrients caused an acceleration of both decay (as measured by weight loss) and increase in nitrogen concentration during the early stages of burial of untreated blocks of both lime and pine. However, statistical analysis of the weight loss data for untreated lime and pine (Table 2.3) showed no significant differences between the rates of decay of centre and surface blocks of either wood type, although there were significant differences in absolute weight loss between the surface and centre wood blocks. Statistical analysis of the nitrogen data for untreated lime and pine blocks (Table 2.4) showed a significant difference in the rate of nitrogen increase between surface and centre blocks of pine but no significant difference for lime. However, there were significant differences in absolute nitrogen content between centre and surface blocks of both wood types. Waite and King (*op cit*) observed that the effect of surface nutrients on decay and nitrogen increases of lime blocks were most pronounced during the

early stages of soil burial. Their burial experiment included analysis of wood blocks exhumed at weekly intervals during the first three weeks, thus the effects of surface nutrients on rates of decay and nitrogen increase may have been more apparent in their work than in this experiment. The presence of surface nutrients would be expected to act as an early stimulus to decay by enhancing the chemostimulation of soil microflora, leading to a more rapid microbial invasion of the wood than would occur in centre wood. The resultant larger microbial biomass in the surface wood should accelerate decay. Also, surface nutrients present in wood raise the nitrogen content closer to the 0.2% $\frac{w}{w}$ threshold (Levi and Cowling, *op cit*) above which soft-rot decay can occur, thus allowing decay to commence more quickly than in wood with low concentrations of soluble nutrients.

CCA treated blocks of all wood types showed increases in nitrogen content during soil burial (Figs 2.2 - 2.4). These increases followed a similar pattern to those observed in untreated wood and the rate of increase in nitrogen content was not greatly depressed by the presence of CCA, except where decay did not occur, in which case early nitrogen increases were not sustained. King, Smith, Baecker and Bruce (1981) observed no increases in the nitrogen content of hardwood blocks treated to above toxic thresholds with CCA. However, the CCA concentrations required to prevent decay in their studies were higher than

those used in blocks which remained undecayed in this experiment. Their undecayed blocks may therefore have contained sufficient CCA for leach losses of preservative to sterilise the surrounding soil and prevent microbial invasion of the wood.

In contrast with the nitrogen data, weight loss data (Figs 2.2 - 2.4) show that CCA greatly depressed the rate of decay and increased the length of the induction phase i.e. the period before significant decay occurred. Thus, at the end of the induction phase, the nitrogen content was higher in CCA treated than in untreated wood. These findings suggest that microbial invasion occurs in treated wood at a rate similar to that observed in untreated wood.

The length of the induction phase may be greater in CCA treated wood due to a requirement for higher microbial or nutrient levels than those required in untreated wood before decay can commence. The considerable nitrogen increases observed in CCA treated wood at low decay levels suggests that a sacrificial invasion is occurring: micro-organisms invading the wood as a result of chemostimulation are killed by active soluble preservative elements and, upon autolysis, enhance the wood nutrient content. The products of autolysing micro-organisms may complex preservative elements, thus rendering the wood less toxic to subsequent invading

micro-organisms and allowing decay to commence. Consequently, as the CCA treating concentration increases, more micro-organisms and hence higher nitrogen thresholds should be required before decay can commence.

Since wood decay by Basidiomycete fungi is generally inhibited by the presence of CCA, nitrogen increases observed in CCA treated wood in soil may more truly reflect the amount of microbial biomass present than in the case of untreated wood where Basidiomycete fungi may be present without significantly contributing to the total wood nitrogen content.

The presence of surface nutrients in CCA treated wood clearly influenced both decay and nitrogen transfer (Figs 2.2 and 2.4). The toxic thresholds were higher in both lime and pine in the presence of surface nutrients, being 2.0% $\frac{W}{V}$ and over 3.0% $\frac{W}{V}$ CCA for lime centre and RSN blocks respectively and 0.5% $\frac{W}{V}$ and 1.0% $\frac{W}{V}$ for pine centre and RSN blocks respectively. Statistical analysis of the weight loss data (Table 2.3) shows that the presence of surface nutrients significantly increased the rate of decay in both pine and lime at all CCA treatment levels. These findings confirm those of King, Smith, Baecker and Bruce (*op cit*) for lime. However, they also show, for the first time, that surface nutrients influence the performance of a CCA treated softwood, pine.

The rate of increase in nitrogen content was also significantly higher in CCA treated pine and lime blocks containing surface nutrients than in matched centre wood blocks (Table 2.4). The presence of surface nutrients clearly has a similar effect in CCA treated wood as in untreated wood, providing an early stimulus to microbial invasion of the treated wood, as shown by accelerated nitrogen increases and leading to the earlier establishment of threshold microbial or nutrient levels for decay. Also, the higher nitrogen concentration of CCA treated wood containing surface nutrients may reduce the toxicity of the preservative, as demonstrated by Henningsson (1976) for wood with added nitrogen.

Comparison of the weight loss data for the CCA treated hardwoods (Figs 2.2 and 2.3) and CCA treated pine (Fig 2.4) clearly shows that the toxic thresholds of CCA were far higher in lime and beech than in pine. Pine centre was protected by 0.5% $\frac{W}{V}$ CCA whereas lime centre was protected by 2% $\frac{W}{V}$ CCA and beech was not protected by 3.0% $\frac{W}{V}$ CCA. In the presence of surface nutrients, pine was protected by 1.0% $\frac{W}{V}$ CCA whereas lime was not protected by 3.0% $\frac{W}{V}$ CCA. The rate of increase in nitrogen content was also lower in CCA treated pine than in the CCA treated hardwoods, regardless of the presence or absence of surface nutrients, showing the same pattern as in the untreated woods. The differing rates of nitrogen increase in different wood types may relate to the effects of the individual wood

species on the soil microflora, probably with respect to the wood's chemostimulatory nature. King and Waite (1979) suggested that if the larger nitrogen increases they observed in hardwoods than softwoods were as a result of a larger microbial presence in the hardwoods, more preservative should be required to protect hardwoods than softwoods.

Comparison of CCA retentions of blocks calculated from liquid uptake values and analytical data (Appendix I) show that discrepancies existed between the retentions calculated by the two methods. Selective absorption ratios (Table 2.7) show that the analytical values for copper chromium and arsenic generally exceeded the liquid uptake values. This pattern of selective absorption during impregnation has previously been noted (Smith and Williams, 1973b; Henshaw, 1979; King, Smith, Baecker and Bruce, *op cit*) and may be caused by adsorption of preservative elements onto cation exchange sites in wood or by chemical reactions with the wood. This would lead to a fall in the concentration of preservative elements in liquid within the wood blocks, thus setting up diffusion gradients bringing further preservative elements into the wood. This hypothesis is supported by the fact that the ratio generally decreased with increasing CCA treating concentration since saturation of all reaction sites in the wood should occur as the CCA concentration increases. The ratios observed in this experiment were lower than those observed by Henshaw (*op cit*). However, he studied

this effect in thin veneers with a much larger surface area to volume ratio than the blocks used in this experiment, thus allowing more rapid diffusion of further elements into the wood substance. In addition, the use of only a five minute soaking of blocks in the CCA solution in the current experiment considerably reduced the opportunity for diffusion of preservative elements into the blocks. This was demonstrated by King, Smith, Baecker and Bruce (*op cit*) who found that the selective absorption ratios of both copper and chromium increased as the period of soaking of blocks in CCA solutions during impregnation was increased from 5 to 120 minutes. Some of the ratios for beech and lime in this experiment were below a value of one (i.e. the liquid uptake value exceeded the analytical value). A possible explanation for this is that, during impregnation, water penetrates the wood fibres from vessels and rays more rapidly than the preservative elements which may be screened from penetrating fibres by preservative fixed to the vessel or ray cell walls or the lumina of individual fibres. Such a problem could be further aggravated by the short impregnation time with water penetrating all wood fibres fully but preservative elements having little time to diffuse throughout the wood. Incomplete penetration of softwood blocks by preservative elements is less likely since passage of the preservative solution through the wood during impregnation is mainly via the tracheids.

The analytical preservative data (Figs 2.5 - 2.10) show that, during soil burial, the concentrations of all three toxic elements apparently fell in all wood types at treating concentrations of less than 3.0% $\frac{W}{V}$ CCA. Analyses of variance (Table 2.8) showed that losses of copper, chromium and arsenic were generally significant in CCA treated pine at all treating concentrations. The results for lime were more variable, but significant losses of copper occurred at all CCA treating concentrations up to 2.0% $\frac{W}{V}$. These losses may represent an unfixed portion of the preservative, existing in the treated wood in the form of soluble salts. Such unfixed preservative should be highly susceptible to leaching from the wood into the surrounding soil. This view is supported by the fact that percentage losses of preservative elements (Table 2.6) fell as the CCA treating concentration increased, since the proportion of CCA fixed to wood generally increases with increasing CCA treatment level (Dahlgren, 1975b). It is also possible that some of the losses of preservative elements observed in this experiment may have been caused by the action of the soil environment on the preservative fixed to the wood: CCA gradually solubilised from fixation sites on the wood by the soil water and its constituents might be taken up by the cation exchange sites in the adjacent soil. In addition, a fungal presence in the wood, as demonstrated by the elevated nitrogen levels, may solubilise some preservative, as described by Levi (1976). Since the pH

of the soil was close to neutral, it is unlikely that the acidity of the soil in itself could have caused significant solubilisation of preservative.

Figs 2.5 - 2.10 suggest that the presence of surface nutrients in wood was associated with lower preservative stability. However, two-way analyses of variance of the preservative data (Table 2.8) detected no significant difference in losses of preservative elements between surface and centre wood of either lime or pine. T-tests of the data (Table 2.9) did detect significant differences between toxic element contents of centre and surface blocks of both lime and pine at the end of the burial period. Such differences were generally not significant in unburied control blocks, suggesting that losses of preservative elements were increased by the presence of surface nutrients. Such an effect could be caused either by complexing of some preservative to soluble nutrients, rendering it susceptible to leaching, or by the increased microbial biomass present in wood containing surface nutrients, leading to greater solubilisation of preservative.

Most of the preservative losses observed from CCA treated blocks occurred during the first three to six weeks of burial in soil (Figs 2.5 - 2.10). This finding also suggests that the losses represented unfixed preservative elements present in the wood on burial. After six weeks of burial, further losses of preservative elements appeared to be negligible despite considerable

decay in many of the CCA treated wood blocks. Thus, as the amount of remaining wood substance fell during decay, the effective concentration of the preservative in the remaining wood increased. Poor micro-distribution of CCA in the wood blocks could result in this pattern of CCA concentration changes during the decay process in soil: decay in lime and beech blocks could be confined to wood fibres not protected by preservative, whilst well treated portions of the wood might be protected. However, increases in the effective concentration of preservative during decay were not confined to the hardwoods studied and micro-distribution problems are unlikely in the softwood pine, especially in the small dimensioned blocks used in this experiment. In addition, the same pattern of preservative losses was observed at very low treatment levels which could not have been sufficient to prevent decay in any portions of the wood, as demonstrated by the very high weight loss figures reached by the end of the burial period. A more probable explanation of the above pattern of preservative losses is that the CCA is either fixed mainly to a portion of the wood not highly susceptible to soft-rot decay, such as lignin (as suggested by Pizzi, 1982) or, if solubilised during decay, becomes complexed to microbial remains within the wood.

Since lignin remains largely undecayed during soft-rot decay of wood, CCA bound to lignin is not likely to be in a soluble available form in the cellulose layers in which soft-rot decay is most prevalent. Thus, if the only

stable complex formed by CCA is with the lignin fraction, protection of wood against soft-rot by CCA is unlikely to be due to toxicity alone. The frequent isolation of fungal mycelium from wood treated with CCA to well above toxic thresholds (Hulme and Butcher, 1977b) and the complete protection of pine at levels considerably sub-toxic in lime and beech, in this experiment, also support this view. Protection may be achieved by the preservative forming a physical barrier to decay by binding to lignin in the S_3 layer of wood cells and masking T-branch initiation sites, as postulated by Butcher and Nilsson (1982). This mechanism might partially account for the better performance of CCA treated softwoods than CCA treated hardwoods since softwoods generally contain more lignin than hardwoods.

If the hypothesis of Butcher and Nilsson is correct, highly decay susceptible, low lignin woods could only be protected from soft-rot decay by CCA if the concentration of preservative within the cellulose fraction, especially the S_2 layers, were high enough to be directly toxic to micro-organisms. Hulme and Butcher (1977c) demonstrated that decay susceptible hardwoods can be protected in laboratory studies, provided that high enough concentrations of CCA are utilised. In further laboratory studies, Lewis and Brooks (1983) also achieved protection of susceptible hardwoods with high concentrations of CCA. The treated wood specimens were severely leached in a Soxhlet extractor prior to soil exposure but the wood was protected from decay

despite the overall concentration of CCA in the wood after leaching being well below normal toxic thresholds. The authors attributed this effect to "microscreening" of preservative elements: copper, chromium and arsenic entering wood in CCA solution during impregnation becomes fixed preferentially to "passive" sites such as pit structures, cellular inclusions, vessels, rays and fibe S_3/lumen interfaces which they reach prior to "active" sites in the S_2 layers of wood fibres. Therefore, at low CCA treating concentrations, preservative elements do not reach the S_2 cellulose layers in large quantities due to depletion by fixation to passive sites, whereas at higher CCA concentrations, the extra preservative elements compensate for this microscreening and more is deposited on active sites in the S_2 layers. Therefore, if the hypothesis of Lewis and Brooks is correct, protection of hardwoods in soil contact can be achieved by CCA, provided that the treating concentration is high enough to deposit high concentrations of toxic elements into the cellulosic S_2 layers.

If CCA does not produce a stable complex with cellulose in the S_2 layers, protection of hardwoods against soft-rot attack is unlikely to be permanent. McNamara, Triana and Greaves (1981) and Leightley and Norton (1983) have noted that in tropical field situations, where leaching of preservative may be very rapid, eucalypt cannot be protected by concentrations of CCA well above

those found effective by Hulme and Butcher. Smith (1980), in laboratory studies, also found that wood treated with very high concentrations of CCA, after a long induction phase, did decay, although the rate of decay was lower at high treatment levels. Smith considered that the induction phase that he observed was caused by leaching of unfixed preservative from the wood into the surrounding soil with decay commencing once the concentration of soluble preservative elements was small enough to be no longer toxic. It therefore seems unlikely that complete protection of hardwoods by CCA alone will ever be achieved.

This experiment has clearly demonstrated the importance of nutrient availability to the soft-rot decay of CCA treated hardwoods and softwoods in soil and has also demonstrated that considerable transfer of microbial biomass occurs from soil to CCA treated wood. Such microbial invasion may provide an important mechanism for the failure of CCA treated wood, since invasion, possibly caused by chemostimulation of the soil microflora by the wood, is apparently not inhibited by the presence of even comparatively high concentrations of CCA in the wood. The establishment of threshold nutrient levels and the possible solubilisation or immobilsation of CCA by micro-organisms in wood resulting from such an invasion appear to make the eventual failure of CCA treated wood inevitable.

Clearly, CCA treated softwoods, such as pine, generally perform well in soil contact and this may be due both to the lower rate of microbial invasion of such wood, as demonstrated in this experiment and to other factors such as the good macro and microdistribution of the preservative, the lower natural susceptibility of the wood and the possible high degree of protection achieved by lignin bound CCA. The isolated incidence of failure of CCA treated pine posts in New Zealand may also be partially attributed to the high nutrient status of the soil: since this experiment has demonstrated that high nutrient levels in CCA treated pine do increase its decay susceptibility, it may be postulated that a high nutrient availability in the surrounding soil might have a similar effect. The highly fertile horticultural soils on the New Zealand vineyards also had very large microbial populations, and hence transfer of microbial biomass and nutrients to the wood may have been unusually rapid.

Clearly the findings of this experiment cannot be related directly to the field situation but they provide an insight into the mechanisms which may be occurring at the surface of service material and since soft-rot is generally a surface phenomenon in CCA treated wood in soil, processes occurring at the wood surface are most important. Soluble nutrients may be present at the surface of service material, Such large pieces of timber,

particularly transmission poles, have a much smaller surface area to volume ratio than the wood planks used to prepare the blocks for this experiment. Therefore, the concentrations of soluble nutrients could potentially be far higher at the surface of large pieces of timber in service than those which significantly reduced the toxicity of CCA in this experiment. However, normal commercial CCA treatment practice involves soaking the timber in the preservative solution for up to two hours which may remove most of the soluble nutrients from the wood. Any soluble nutrients remaining in the wood after preservative treatment would certainly re-accumulate at the surfaces during curing.

Drysdale (1983) has shown that preservative elements may become redistributed towards the surfaces of CCA treated planks during drying, forming preservative-rich surface profiles. Such profiles present at the surface of CCA treated service material might also play an important role in determining its performance. Such redistributed preservative is likely to be in an unfixed soluble form which should readily leach out of the wood as soon as it is placed in service. This might also significantly influence the processes occurring at the wood/soil interface during the early stages of the service life of timber.

If nutrient rich surface profiles do exist in service material, the findings of this experiment could

have important implications. The presence of surface nutrients in CCA treated service timber in soil would compromise both the stability and toxicity of the preservative in the surface regions, leading to the early onset of soft-rot decay in these regions. Such problems would be particularly serious in wood treated with low concentrations of CCA, since such material is apparently more susceptible to losses of preservative elements. It is therefore essential that tests should now be carried out to establish the importance of soluble nutrients in CCA treated service material. If concentrations of soluble nutrients do accumulate at the surfaces of treated material, their removal by leaching prior to CCA treatment might greatly increase the service life of the timber.

CHAPTER 3

STUDIES OF THE FIXATION PROCESSES AND THE LEACHABILITY OF PRESERVATIVE ELEMENTS IN CCA AND ACA TREATED WOOD

3.1 Introduction

The principal aims of the work described in this chapter were:

1. to determine factors contributing to losses of toxic elements observed from CCA treated wood in the CCA soil burial experiment (Chapter 2).

2. to study the properties of wood treated with an alternative preservative, ammoniacal copper arsenate (ACA) with specific reference to treatment and curing procedures, fixation processes and leachability of preservative elements.

The studies on ACA were undertaken as a preliminary step to a soil burial experiment using ACA treated wood (Chapter 4), the results of which were to be compared directly with those of the CCA burial experiment (Chapter 2) in terms of toxic thresholds of the main fungicide copper.

The results of the CCA burial experiment (Chapter 2) show that losses of preservative elements occur from wood, especially at low preservative treatment levels, in soil. These losses may be due either to simple aqueous leaching of soluble preservative elements from the wood (Smith, 1980) or to leaching supplemented by additional soil factors of a biological or chemical nature.

Fungal presence in CCA treated wood can cause solubilisation of preservative elements (Levi, 1976). Bacteria may also cause solubilisation of CCA in wood and since this group of micro-organisms are primary colonisers of treated wood emplaced in soil (Clubbe and Levy, 1982), such solubilisation could be of considerable importance to the subsequent performance of the wood.

Soil chemical properties may also influence preservative stability. Since low pH increases the leachability of preservative elements from CCA treated wood (McCarthy, 1959), increased losses of CCA from treated wood may occur in highly acidic soils. Hedley (1984) has also demonstrated that high ionic concentrations in soil solutions, such as those in highly fertile agricultural land, influence CCA stability. Organic compounds present in soil may also affect preservative stability in treated wood emplaced in it: organic acids such as humic acid, present in soil solution would be expected to compete with cation exchange sites on the wood for Cu^{2+} and Cr^{3+} ions. Soils with a high clay or humus content and consequently a high cation exchange capacity might also accelerate the loss of Cu^{2+} and Cr^{3+} from CCA treated wood by maximising the concentration gradient between the aqueous phases in the wood and the soil.

It has been demonstrated that relative humidity (Henshaw, 1979) and temperature (Wilson, 1972) during the curing of CCA treated wood influence the length of the optimum period for fixation and premature drying of the timber during curing would cause fixation reactions to cease, leading to incomplete fixation of preservative elements in the wood. Such a problem would lead to poor performance of CCA treated timber in external situations. Dahlgren and Hartford (1972a), using mixtures of sawdust and CCA solutions, showed that reactions in CCA treated wood continue for several months after "fixation" (as determined by leachability) is apparently complete, leading to alternate rises and falls in wood pH. If the products of fixation of CCA to wood do change over a period of months, the moisture content of the wood, even after the initial curing period, may be important in determining the performance of the treated timber in service.

The current British Standard method for curing CCA treated test material (BS6009, 1982) involves a four week curing period. The wet blocks are transferred immediately after impregnation to a sealed vessel, only breaking the seal once every 2 days to turn the wood blocks. The wood blocks are stored in this manner for fourteen days after which the lid of the vessel is gradually removed during the third week and then the blocks are allowed to dry in the open vessel for a further week.

Henshaw (*op cit*) determined that at 20°C and 83% relative humidity, fixation (as determined by leachability) was complete after two weeks. His wood samples were then transferred immediately, without drying, to distilled water and only small proportions (less than 5%) of the preservative elements were removed during a 100 hour leaching procedure. This suggests that the standard procedure of allowing the wood samples to dry for two weeks after the initial curing for two weeks at high relative humidity does not increase the leach resistance of CCA in wood.

The importance of temperature and relative humidity to the rate of fixation of preservative elements to CCA treated wood during curing suggests that differences in the handling of CCA treated wood and weather conditions at commercial impregnation plants at different localities influence the performance of the treated timber in service, with specific reference to preservative stability.

ACA treated wood, in contrast to CCA treated wood, must be allowed to dry after impregnation so that volatile ammonia present after treatment can diffuse and evaporate from the wood. This also ensures that copper and arsenic are precipitated in an insoluble form. In addition, if the extra nitrogen present in ACA treated wood acts as a nitrogen source to wood decaying micro-organisms and thus acts as a stimulus to decay, as suggested by Ruddick (1979), loss of ammonia from ACA treated wood as a result

of drying may be important in minimising decay susceptibility. Therefore, variations in curing and drying regimes for ACA treated wood may considerably influence its performance in service. Dimensions of timber may also influence the rate of loss of nitrogen due to variations in surface area to volume ratio.

The fixation mechanism of ACA to wood contrasts greatly with that of CCA. In CCA, the oxidising dichromate plays an important role in the fixation of copper and arsenic to wood by forming stable complexes with these elements in either the hexavalent or trivalent form and by causing precipitation of these elements as the wood pH rises during reduction of chromium VI to chromium III (Dahlgren, 1972; Pizzi, 1982). In addition, the oxidation of wood by chromium VI may lead to the formation of more carboxylic acid groups in the wood which may act as cation exchange sites allowing cation exchange fixation of Cu^{2+} and Cr^{3+}. The absence of the oxidising dichromate in ACA means that fixation of the copper and arsenic to the wood can only occur either by precipitation reactions e.g. forming copper arsenates as the ammonia is lost from the treated wood during drying, or by cation exchange fixation of copper to existing exchange sites such as the carboxylic acid and phenolic groups of lignin or the carboxyl groups of cellulose. Precipitation reactions may involve the formation of copper hydroxide ($Cu(OH)_2$) and copper arsenates such as $Cu(OH)CuAsO_4$ and

$CuHAsO_4$ as a result of the volatilisation of ammonia during drying and the consequent fall in wood pH. Copper may also complex with cation exchange sites either as Cu^{2+} or as cupprammonium ions ($Cu(NH_3)_4(H_2O)_2^{2+}$). The atom ratio of copper to arsenic in ACA (as used by Hulme and Butcher (1977c)) is 1.61 : 1. In the absence of wood, precipitation of ACA leads to the formation of complexes with varying ratios of copper to arsenic (Hulme, 1979). However, leaching studies on ACA treated wood (Rak, 1976; Wilson, Tamblyn and McCarthy, 1955) have shown large losses of arsenic (up to 50%) and only minimal losses of copper. This suggests that a large proportion of the copper in ACA treated wood is fixed by cation exchange mechanisms.

Smith and Williams (1973b) showed that the selective absorption ratio of copper was higher in ACA treated wood than in CCA treated wood. This may be due, in part, to the differences in fixation mechanisms described above. The absence of chromium from ACA solutions allows adsorption of copper and cupprammonium ions onto cation exchange sites of the wood without competition from trivalent Cr^{3+} ions which are produced during the impregnation of wood with CCA. The alkaline nature of the ACA treating solution also produces pH conditions more favourable for cation exchange of copper. In addition, the improved penetration of the wood by ammoniacal solution may extend cation

exchange fixation of copper during ACA treatment of wood by allowing the preservative to reach more potential fixation sites.

Ruddick (*op cit*) has shown that the nitrogen content of ACA treated wood remains well above that of untreated wood, even after prolonged uncovered storage outdoors. This suggests that some of the ammonia in treated wood is in a form resistant to aqueous leaching, probably either combined with preservative elements in insoluble complexes or complexed as ammonium or cupprammonium ions to cation exchange sites on the wood. If the ammonia complexes with either the toxic elements or cation exchange sites on the wood, there should be a saturation point for ammonium ions in ACA treated wood above which all extra nitrogen is lost either by volatilisation or leaching. Thus, above a certain point, the ammonia concentration of the ACA treating solution should not influence the final nitrogen content of the wood.

Residual ammonium ions remaining in ACA treated wood after curing may influence the wood pH considerably. The pH of the wood in turn will influence the products of fixation of ACA in the wood and the resistance of any complexes or precipitates formed to aqueous leaching. Thus, the fixation of toxic elements and ammonium ions to ACA treated wood may vary from one wood type to another, depending upon the pH of the wood prior to treatment.

Since the fixation of ACA to wood can rely only on cation exchange fixation and precipitation reactions caused by loss of ammonia, there should be no need to maintain the treated wood at a high relative humidity during the early stages of curing to ensure adequate fixation as is the case with CCA treated wood. However, Henningsson, Hager and Nilsson (1981) have shown that wood treated with an ammoniacal copper preservative wrapped in polythene for 21 days prior to drying is more resistant to soft-rot attack in soil than similarly treated wood allowed to air-dry immediately after impregnation. These authors concluded that maintaining a high moisture content in the wood after impregnation had allowed preservative elements to continue to diffuse through the cell walls of wood fibres leading to a better micro-distribution of copper in these fibres than in fibres of treated wood allowed to dry immediately after impregnation.

Aims of Studies

CCA

The stability of CCA in treated wood may be influenced by variations in curing procedures and in soil contact may be further influenced by chemical and biological components of the soil.

Experiments were therefore undertaken to determine:

1. whether the two week air-drying period included in the current British Standard curing procedure is necessary in order to minimise leachability of preservative elements (or maximise fixation).

2. the effect of aqueous extractives of the soil used in the burial experiment (Chapter 2) on the leachability of CCA from wood.

3. the effect of a soil bacterial suspension in an aqueous soil extract on the leachability of CCA from wood.

ACA

There is currently little information on the uptake and fixation of ACA to wood, and, in particular, the role of nitrogen in this fixation.

Experiments were therefore undertaken to determine:

1. the concentration of ammonium nitrogen and total nitrogen in ACA treated wood both before and after leaching in distilled water.

2. the influence of ammonia concentration in an ACA treating solution on the final wood nitrogen content.

3. selective absorption ratios for preservative elements in ACA treated wood.

4. the leachability of preservative elements from ACA treated wood using distilled water.

Additionally, the effect of ACA treatment on the pH of the wood was measured.

Prior to the commencement of the above experiments, preliminary studies were undertaken:

1. Since, after ACA treatment, wood contains volatile ammonia, an experiment was undertaken to determine the period of air-drying required for ACA treated wood blocks to reach a stable nitrogen content. A standard drying procedure for ACA treated wood blocks was subsequently established.

2(a) A procedure was devised to determine the ammonium nitrogen content of wood blocks, using the action of concentrated NaOH on the wood to release ammonia in a Kjeldahl type steam distillation.

(b) A test of the procedure was undertaken to ensure that the concentration of NaOH used was sufficient to release all free ammonia from the wood blocks.

(c) An experiment was also undertaken to determine whether or not amino acids, often present in significant amounts in wood (Laidlaw and Smith, 1965), release sufficient ammonia, when subjected to NaOH, to contribute significantly to the ammonium nitrogen analysis of wood blocks.

3. Since wood analysed for ammonium nitrogen content was no longer suitable for total nitrogen and copper analysis, a procedure was devised for homogenising and then dividing individual wood blocks into two portions so that both ammonium nitrogen and total nitrogen/copper analyses could be performed on every block. The procedure was evaluated for reproducibility prior to adoption for the burial experiment.

3.2 Materials, Methods and Results

3.2.1 Preparation of wood blocks, preservative solutions and treatment procedures

3.2.1.1 Preparation of wood blocks

Centre wood blocks (10 x 10 x 5 mm) with large (10 x 10 mm) radial faces were prepared from the sapwood region of oven dried planks of the species lime (*Tilia vulgaris*, Hayne), pine (*Pinus sylvestris*, L) and spruce (*Picea sitchensis*, Carr) as previously described (Chapter 2).

Blocks were labelled, dried at 102°C for three hours and weighed.

3.2.1.2 Preparation of preservative solutions

Analar grade reagents, grade A glassware and distilled water were used throughout these experiments.

CCA

3.0 and 5.0% $\frac{W}{V}$ solutions of a CCA type C formulation (BS4072, 1974) were prepared (see Chapter 2, Section 2.2.2).

ACA

A stock solution of 1·42% $\frac{W}{V}$ ACA was prepared according to the method of Hulme and Butcher (1977c)

except that $As_2O_5.2H_2O$ was replaced by $As_2O_5.5H_2O$. 14.168 g of $As_2O_5.5H_2O$ was dissolved in a mixture of 100 cm^3 of 0.880 ammonia solution and approximately 300 cm^3 of distilled water. 16.484 g of basic copper carbonate ($CuCO_3.Cu(OH)_2.H_2O$) was then added and the mixture stirred until dissolved. The solution was then made up to 2 litres in a volumetric flask with distilled water.

The stock solution contained 1.35% $\frac{W}{V}$ ammonia and 4.45 g/litre of copper (equivalent to a 5% $\frac{W}{V}$ CCA solution). It was subsequently diluted with distilled water and ammonia solution to give the required range of copper concentrations whilst maintaining the ammonia concentration at 1.35% $\frac{W}{V}$. The addition of ammonia was necessary to avoid precipitation of copper hydroxide. A 1.35% $\frac{W}{V}$ aqueous ammonia solution was also prepared.

3.2.1.3 Analysis of preservative solutions

CCA solutions were analysed for copper, chromium and arsenic contents and ACA solutions were analysed for copper, arsenic and ammonia content. The 1.35% $\frac{W}{V}$ ammonia solution was also analysed for ammonia content.

Copper, chromium and arsenic were analysed using an A.A.S. standard additions technique (Chapter 2). Ammonia was analysed in a Markham distillation unit by the Kjeldahl technique.

3.2.1.4 Impregnation and curing of blocks

The impregnation procedure for both CCA and ACA treated wood was carried out following the method of BS6009 (1982) except that the blocks were soaked for 30 minutes in the preservative solution: uptake of CCA solution and selective absorption of copper by wood blocks of these dimensions do not increase significantly after thirty minutes of soaking (King, Smith, Baecker and Bruce *op cit*). Since the ammonia in ACA solutions may increase the rate of penetration of preservative solution through wood, the same time period was also used for the ACA preservative.

The treated blocks were patted dry with tissue paper to remove excess liquid and weighed wet. They were then cured for two weeks in sealed petri-dishes containing moistened tissue paper and were turned once daily by inverting the petri-dish. The effects of different subsequent drying regimes for the treated blocks were investigated.

3.2.2 Leaching studies on CCA treated wood

3.2.2.1 The effect of air-drying on the leachability of CCA from treated wood

Fifteen centre wood blocks of both lime and pine were impregnated with a 3% $\frac{w}{v}$ CCA solution and cured wet

for two weeks as described above. Five blocks of each wood type were then removed for immediate leaching. The tissue paper was removed from the petri-dish and the lid replaced. During the following seven days, the lid was gradually removed and the remaining blocks were then left in the open petri-dish for a further seven days. This air-drying procedure is identical to that of BS6009 (1982).

Aqueous leaching of treated blocks

The procedure described here is a modification of the method of Wilson, Tamblyn and McCarthy (1955) using daily changes of the leach liquor in order to monitor loss of preservative elements with time.

Blocks were leached in groups of five in 1 litre beakers containing 200 cm^3 of distilled water (pH 7.5) stirred magnetically at 25 ± 1°C. Asbestos mats were placed underneath the beakers to prevent the heat produced by the stirrer motors from raising the temperature of the leach liquors.

The leaching was continued for six days and the water was changed daily. The six daily leach liquors for each experiment were stored separately for individual analysis.

Five of the dried blocks and the five undried blocks of each wood type were leached using the above procedure. The remaining five dried blocks of each wood type were chemically analysed without leaching.

Analysis of wood blocks and leach liquors

All leached and unleached blocks and leach liquors were analysed individually for copper and chromium concentrations.

Blocks were digested in A.R. concentrated H_2SO_4 and "100 volume" H_2O_2 (Chapter 2, Section 2.2.7.1). The digests were diluted and analysed for copper and chromium using a standard additions technique on an AAS (Chapter 2, Section 2.2.7.3).

Leachates were acidified with 10 cm^3 of 2.5M H_2SO_4, filtered, diluted and then analysed in the same way.

Results

Mean % $\frac{w}{w}$ analytical concentrations of copper and chromium in unleached control blocks and in air-dried and undried blocks subsequently exposed to aqueous leaching are presented in Table 3.1.

Table 3.1

Mean % $\frac{w}{w}$ copper and chromium concentrations (± standard deviations) in air-dried and undried 3% $\frac{w}{v}$ CCA treated lime and pine blocks before and after aqueous leaching

Wood Type	% $\frac{w}{w}$ Copper			% $\frac{w}{w}$ Chromium		
	Unleached	Leached Undried	Leached Air-dried	Unleached	Leached Undried	Leached Air-dried
Lime	0.391± 0.0047	0.338± 0.123	0.342± 0.071	0.867± 0.089	0.885± 0.089	0.890± 0.107
Pine	0.420± 0.021	0.384± 0.033	0.377± 0.028	0.935± 0.076	0.931± 0.075	0.929± 0.064

From the analytical data for the leached and unleached blocks (Table 3.1), aqueous leaching for 6 days clearly reduced the concentration of copper in both undried and dried blocks of both lime and pine but did not significantly affect the chromium concentration. Mean chromium concentrations in leached lime blocks were apparently higher than in the unleached control blocks, although the large standard deviations make such differences negligible.

For leached blocks, there were no clear differences in either copper or chromium concentration between blocks which had been air-dried or undried prior to aqueous leaching.

Preservative element contents of unleached control blocks were also calculated from preservative uptake data.

Selective absorption ratios for copper and chromium in lime and pine blocks were then calculated. These ratios are presented in Table 3.2

Table 3.2

Selective absorption ratios for copper and chromium in 3% $\frac{W}{V}$ CCA treated lime and pine blocks

Wood Type	Selective Absorption Ratio	
	Copper	Chromium
Lime	1.009	1.256
Pine	1.005	1.252

Selective absorption ratios for chromium were higher than those for copper in both lime and pine blocks and selective absorption ratios for the preservative elements were almost identical in the two wood types.

Total amounts (in µg) of preservative elements in the six daily leachates of the dried and undried CCA treated lime and pine blocks are presented graphically in Figs 3.1 and 3.2 for copper and chromium respectively. Quantities of both preservative elements were highest in the first day leachates and decreased gradually during subsequent days. However, even the sixth daily leachates contained some preservative elements, especially copper. Therefore preservative losses from CCA treated blocks were continuing to occur after six days of aqueous leaching

Fig 3.1 TOTAL MICROGRAMS OF COPPER IN DAILY LEACHATES FROM 3% $\frac{w}{v}$ CCA TREATED LIME AND PINE BLOCKS DURING AQUEOUS LEACHING

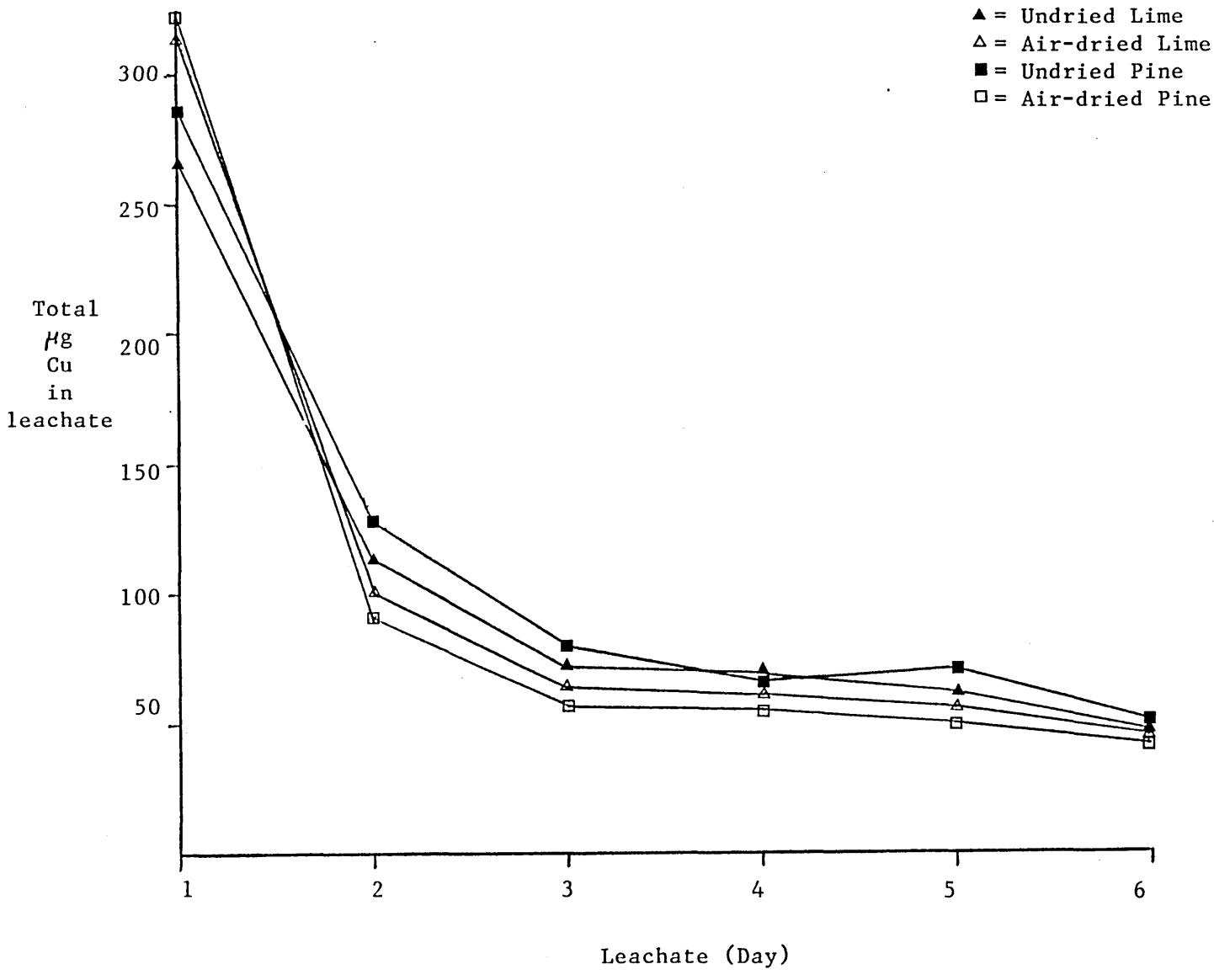
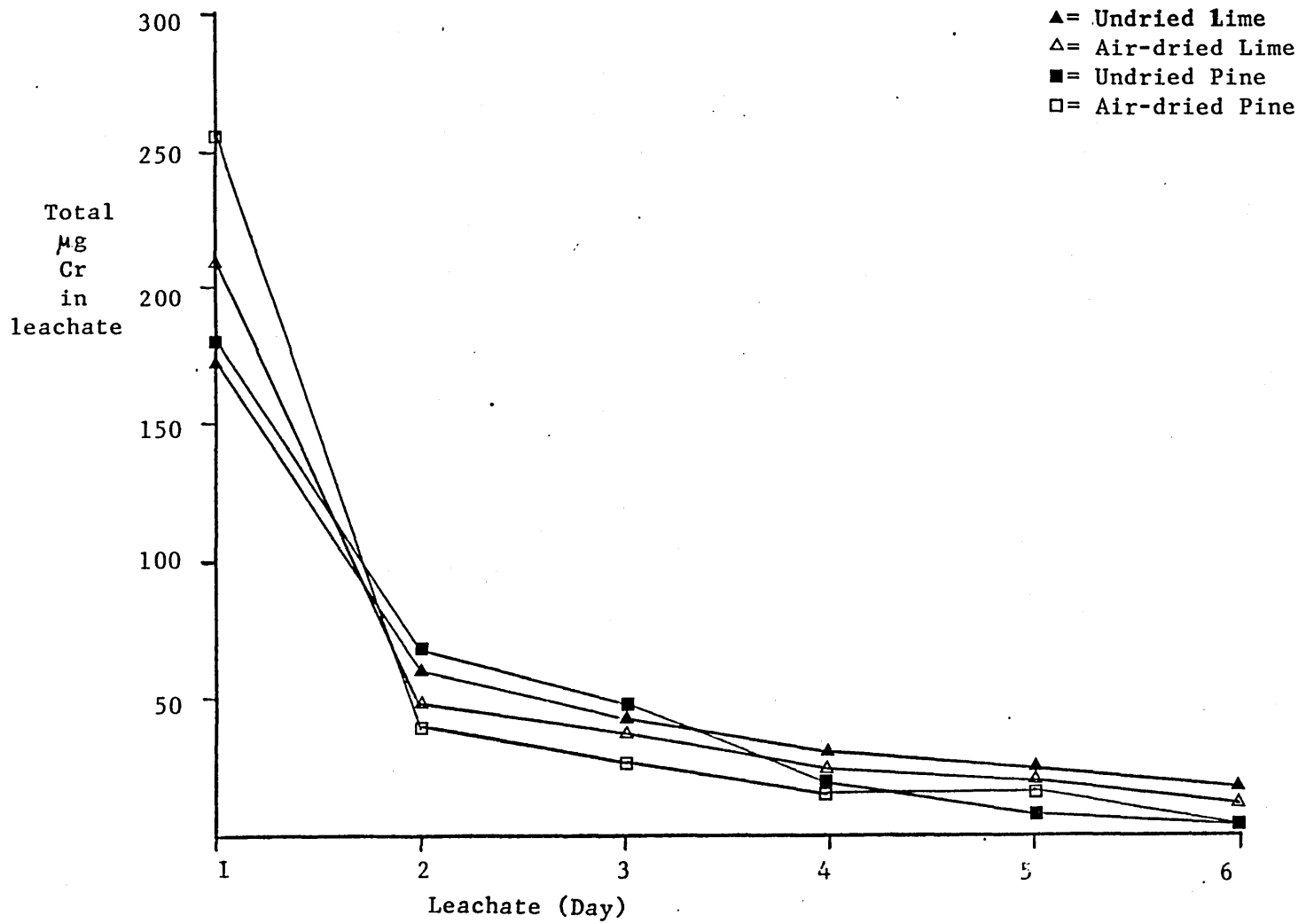


FIG 3.2 TOTAL MICROGRAMS OF CHROMIUM IN DAILY LEACHATES FROM 3%$^{w}_{v}$ CCA TREATED LIME AND PINE BLOCKS DURING AQUEOUS LEACHING



and extrapolation of the curves of Fig 3.1 suggest that losses of copper, at a low level, might continue for considerably more than six days.

Percentage loss of copper and chromium during aqueous leaching

Percentage loss of preservative elements during aqueous leaching of blocks can be calculated by comparing analytical concentrations of the elements in leached blocks and unleached control blocks. However, this method of calculating percentage loss is subject to errors caused by variation in preservative uptake between blocks, such errors being particularly significant where preservative losses are small. This is well illustrated by the CCA treated lime blocks used in the present experiment where the chromium contents of leached blocks were apparently higher than those of unleached control blocks (Table 3.1) despite the fact that analysable quantities of chromium were detected in all of the daily leachates. Therefore, percentage losses of preservative elements were calculated using analytical concentrations of copper and chromium in leached blocks and in leachates, as described below:

The pre-leaching preservative contents of leached blocks were calculated by adding the total µg of copper and chromium in the six daily leachates to the total µg in blocks after leaching (determined by wood block analysis).

Since the leachates contained the preservative elements for five blocks, mean values only could be calculated. Percentage loss of the preservative elements from blocks during aqueous leaching was calculated by expressing the total µg of copper and chromium in the leachates as a percentage of the total µg in blocks prior to leaching.

The percentage losses of copper and chromium from the CCA treated lime and pine blocks during aqueous leaching are shown in Table 3.3.

Table 3.3

Percentage loss of copper and chromium from 3% $\frac{w}{v}$ CCA treated lime and pine blocks during a 6 day aqueous leaching programme

Wood Type	Preservative Element	Blocks dried or not dried after curing	% loss of Cu/Cr during leaching
Lime	Cu	Not	11.72
	Cr	Dried	2.36
Lime	Cu	Dried	10.78
	Cr		2.45
Pine	Cu	Not	12.51
	Cr	Dried	3.83
Pine	Cu	Dried	11.24
	Cr		2.84

The inclusion of a two week drying period in the curing of blocks made no significant difference to the losses of copper and chromium observed.

Aqueous leaching removed a similar amount of copper and of chromium in all cases with no significant differences between lime and pine blocks. However, a higher proportion of copper was lost than of chromium (approximately 12% of the copper but only about 3 to 4% of the chromium).

3.2.2.2 The effects of aqueous soil extracts and bacterial suspensions on the leachability of CCA from treated wood

Lime and pine centre wood blocks treated with 3 and 5% $\frac{w}{v}$ CCA solutions were subjected to a six day leaching procedure using one of three types of leach liquor:

distilled water

an aqueous soil extract

a bacterial suspension in an aqueous soil extract

Table 3.4 shows the number of wood blocks of each type and treating concentration leached with each leach liquor.

Table 3.4

The number of replicate lime and pine centre blocks at each CCA treating concentration leached with each type of leach liquor

Leached for 6 days in	Lime 3% $\frac{w}{v}$ CCA	Lime 5% $\frac{w}{v}$ CCA	Pine 3% $\frac{w}{v}$ CCA	Pine 5% $\frac{w}{v}$ CCA
Unleached control	5	5	5	5
Distilled water	15	15	15	15
Aqueous soil extract	15	15	15	15
Bacterial suspension	15	15	15	15

Three groups of five blocks of each wood type/ treating concentration were leached with each leaching solution.

Impregnation and curing of wood blocks

Fifty centre wood blocks of lime and fifty centre wood blocks of pine were impregnated with each of 3 and 5% $\frac{w}{v}$ CCA solutions and were cured wet for two weeks in petri-dishes (see Section 3.2.1.4). The blocks were then air-dried for two weeks in the petri-dishes, following the procedure outlined in Section 3.2.2.1.

Preparation of aqueous soil extracts

The method described here is a modification of the preparation method for saturation soil extracts described by Hesse (1971).

Soil identical to that used in Chapter 2 (Section 2.2.5) was sieved to 5 mm to remove coarse gravel and then transferred to plastic boxes (260 x 200 x 100 mm). Distilled water was applied evenly to the soil surface and the soil was mixed with a hand trowel. Further distilled water was added and mixed into the soil until it was fully saturated. Saturation was considered complete when the soil was in the form of a thick slurry and the soil surface glistened due to surface water. The boxes of saturated soil were then allowed to stand for 4 hours. The soil was then transferred to 1 litre plastic centrifuge jars with screw tops and was centrifuged at 2500 r.p.m. for 20 minutes. The almost clear solution was decanted from the tops of the jars and the soil discarded.

The aqueous soil extract was vacuum filtered until clear and stored at $4^{o}C$ prior to use.

Preparation of bacterial suspensions in aqueous soil extracts

Bacterial suspensions were prepared by allowing a large bacterial population to build up in some of the aqueous

soil extract prepared as described above. Soil extract to be used for this purpose was removed from cold storage 4 days prior to the commencement of leaching and was stored at room temperature. Bacterial numbers in the solution were determined at the start of the experiment by means of a bacterial counting chamber.

Most of the bacteria present in the extract were found to be Gram positive long rods but there were also small numbers of Gram negative short rods.

Leaching of wood blocks

The leaching procedure was identical to that used in the previous experiment (Section 3.2.2.1). Blocks were leached in groups of five in 200 cm^3 of distilled water, aqueous soil extract or bacterial suspension for 6 days. The solution was changed daily and individual daily leachates were stored separately.

Analysis of wood blocks and leach liquors

Wood blocks were analysed individually for copper, chromium and arsenic concentrations (Chapter 2, Section 2.2.7.3).

Distilled water leachates were acidified, filtered and analysed for copper, chromium and arsenic (Section 3.2.2.1).

Aqueous soil extract and bacterial suspension leachates were digested with sulphuric acid and hydrogen peroxide to break down bacterial remains which might otherwise complex preservative elements. The leachates were acidified by adding 20 cm^3 of 2.5M sulphuric acid and were heated in conical flasks on a hotplate until the total volume of solution had been reduced to approximately 20 cm^3, 10 cm^3 of "100 volume" H_2O_2 was then added to each flask and heating was continued until the volume had again been reduced to 20 cm^3. The addition of hydrogen peroxide and boiling down to 20 cm^3 was then repeated. The digested leachates were then allowed to cool and were then diluted to 100 cm^3 and analysed as described above.

Arsenic concentrations in the leachates were too low to be detected by AAS analysis and arsenic concentrations were therefore only determined for leached and unleached wood blocks.

Results

The mean % $\frac{w}{w}$ copper, chromium and arsenic concentrations in unleached control blocks and in blocks leached with each type of leach liquor are presented in Table 3.5. Copper and arsenic concentrations were invariably lower in leached blocks than in unleached controls but there were no obvious differences in the concentrations of these

elements between blocks leached with the three different leach liquors. Chromium concentrations were not significantly reduced by leaching with any type of liquor and in some cases the chromium concentrations in leached blocks exceeded those in unleached controls.

Selective absorption ratios for each preservative element were calculated for each individual unleached control block using the analytical preservative data and preservative contents derived from the uptake of CCA solution by blocks (Chapter 2, Section 2.3.3). The mean ratios of each preservative element for both lime and pine treated with 3 and 5% $\frac{W}{V}$ CCA solutions are presented in Table 3.6. With the exception of copper data in lime and pine blocks treated with 5% $\frac{W}{V}$ CCA, all selective absorption ratios exceeded one. For both lime and pine blocks at both treating concentrations, the ratios were highest for arsenic and lowest for copper. For both wood types, the ratios for each element were higher in blocks treated with 3% $\frac{W}{V}$ CCA than in blocks treated with 5% $\frac{W}{V}$ CCA.

Percentage loss of preservative elements

Percentage losses of copper, chromium and arsenic from 3 and 5% $\frac{W}{V}$ CCA treated lime and pine blocks during leaching with distilled water, aqueous soil extract or a bacterial suspension in an aqueous soil extract are presented in Table 3.7. Copper and chromium losses were calculated using the analytical preservative contents of

leachates and leached blocks (see Section 3.2.2.1). Arsenic losses were calculated from mean analytical preservative contents of leached and unleached blocks.

For lime and pine blocks treated with either 3 or 5% $\frac{W}{V}$ CCA, neither an aqueous soil extract nor a bacterial suspension removed a significantly higher percentage of copper, chromium or arsenic during leaching than did distilled water. However, percentage losses of copper were invariably slightly higher from blocks leached with aqueous soil extract or bacterial suspension than from identical blocks leached with distilled water.

Percentage losses of copper and chromium were slightly lower from blocks treated with 5% $\frac{W}{V}$ CCA than from blocks treated with 3% $\frac{W}{V}$ CCA. Losses of chromium were invariably low (less than 2.5%). Copper losses ranged from about 9% to nearly 13%. Percentage losses of arsenic from blocks generally exceeded those of copper and chromium and ranged from about 10% to 14.63%. A similar percentage of each preservative element was lost from blocks of each wood type at each treating concentration.

Table 3.5

Mean % $\frac{w}{w}$ copper, chromium and arsenic concentrations in 3 and 5% $\frac{w}{v}$ CCA treated lime and pine blocks before and after 6 days of leaching in distilled water, aqueous soil extract or a bacterial suspension

Wood Type	% $\frac{w}{v}$ CCA	Leach Liquor	Preservative Content (% $\frac{w}{w}$)		
			Copper	Chromium	Arsenic
Lime	3	Unleached	0.380 ±0.020	0.785 ±0.080	0.705 ±0.051
"	3	Distilled Water	0.342 ±0.031	0.787 ±0.075	0.607 ±0.067
"	3	Aqueous Soil Extract	0.347 ±0.018	0.792 ±0.081	0.617 ±0.071
"	3	Bacterial Suspension	0.340 ±0.022	0.784 ±0.062	0.618 ±0.129
"	5	Unleached	0.572 ±0.037	0.835 ±0.102	0.801 ±0.101
"	5	Distilled Water	0.518 ±0.031	0.842 ±0.088	0.694 ±0.089
"	5	Aqueous Soil Extract	0.519 ±0.029	0.837 ±0.093	0.709 ±0.095
"	5	Bacterial Suspension	0.509 ±0.025	0.828 ±0.077	0.668 ±0.062
Pine	3	Unleached	0.435 ±0.023	0.908 ±0.077	0.714 ±0.032
"	3	Distilled Water	0.349 ±0.031	0.862 ±0.059	0.661 ±0.058
"	3	Aqueous Soil Extract	0.343 ±0.017	0.901 ±0.071	0.692 ±0.083
"	3	Bacterial Suspension	0.346 ±0.019	0.889 ±0.046	0.650 ±0.061
"	5	Unleached	0.601 ±0.046	1.191 ±0.122	0.959 ±0.048
"	5	Distilled Water	0.549 ±0.038	1.162 ±0.081	0.838 ±0.071
"	5	Aqueous Soil Extract	0.542 ±0.042	1.183 ±0.060	0.848 ±0.090
"	5	Bacterial Suspension	0.544 ±0.038	1.217 ±0.083	0.823 ±0.074

Table 3.6

Selective absorption ratios (± standard deviation) for copper, chromium and arsenic in 3 and 5% $\frac{W}{V}$ CCA treated lime and pine blocks

Wood Type	% $\frac{W}{V}$ CCA	Selective Absorption Ratios		
		Copper	Chromium	Arsenic
Lime	3	1.029 ±0.150	1.234 ±0.165	1.465 ±0.172
"	5	0.998 ±0.081	1.135 ±0.156	1.309 ±0.150
Pine	3	1.020 ±0.107	1.208 ±0.122	1.414 ±0.168
"	5	0.982 ±0.101	1.088 ±0.134	1.277 ±0.144

Table 3.7

Percentage loss of copper, chromium and arsenic (± standard deviations) from 3 and 5% $\frac{W}{V}$ CCA treated lime and pine blocks during leaching with distilled water, aqueous soil extract or a bacterial suspension in an aqueous soil extract

Wood Type	% $\frac{W}{V}$ ACA	Leach Liquor	Percentage Loss		
			Copper	Chromium	Arsenic
Lime	3	Distilled Water	11.04 ±0.89	2.18 ±0.24	14.63
"	3	Aqueous Soil Extract	12.54 ±0.91	1.99 ±0.18	12.87
"	3	Bacterial Suspension	12.69 ±0.97	2.28 ±0.15	14.55
"	5	Distilled Water	8.97 ±0.76	1.48 ±0.14	12.03
"	5	Aqueous Soil Extract	9.66 ±0.58	1.63 ±0.17	12.14
"	5	Bacterial Suspension	10.11 ±0.92	1.47 ±0.28	13.76
Pine	3	Distilled Water	11.18 ±0.80	1.94 ±0.18	11.41
"	3	Aqueous Soil Extract	12.33 ±0.78	2.01 ±0.31	10.22
"	3	Bacterial Suspension	12.10 ±0.99	1.86 ±0.21	12.39
"	5	Distilled Water	9.15 ±0.52	1.28 ±0.19	11.70
"	5	Aqueous Soil Extract	9.21 ±0.65	1.36 ±0.24	11.54
"	5	Bacterial Suspension	9.79 ±0.47	1.20 ±0.16	13.27

3.2.3 Studies on ACA treatment and ACA treated wood

A series of preliminary experiments was undertaken to:

1. determine the period of air-drying required for ACA treated blocks to reach a stable nitrogen content;

2. devise a procedure to determine the ammonium nitrogen content of wood blocks;

3. ensure that the concentration of NaOH used in the procedure devised above was sufficient to release all free ammonia from wood blocks;

4. determine whether or not amino acids in wood could contribute significantly to the ammonium nitrogen analysis of wood blocks;

5. devise an analytical procedure allowing the analysis of each individual block for total nitrogen, copper and ammonium nitrogen. The procedure devised was tested for reproducibility of results.

3.2.3.1 Standardisation of drying procedure for ACA treated wood blocks

Forty five centre wood blocks of lime were impregnated with a 0.566% $\frac{W}{V}$ ACA solution and cured in sealed petri-dishes for two weeks (Section 3.2.1.4).

Five blocks were then analysed immediately for nitrogen content by a micro-Kjeldahl technique (Chapter 2).

The remaining 40 blocks were placed in a fan oven at 25°C to dry in an open petri-dish. Five blocks were removed from the oven every seven days over an eight week period and analysed for nitrogen content (Chapter 2).

Results

The mean nitrogen contents and standard deviations of ACA treated wood blocks both before and during air-drying are shown in Table 3.8 and graphically in Fig 3.3.

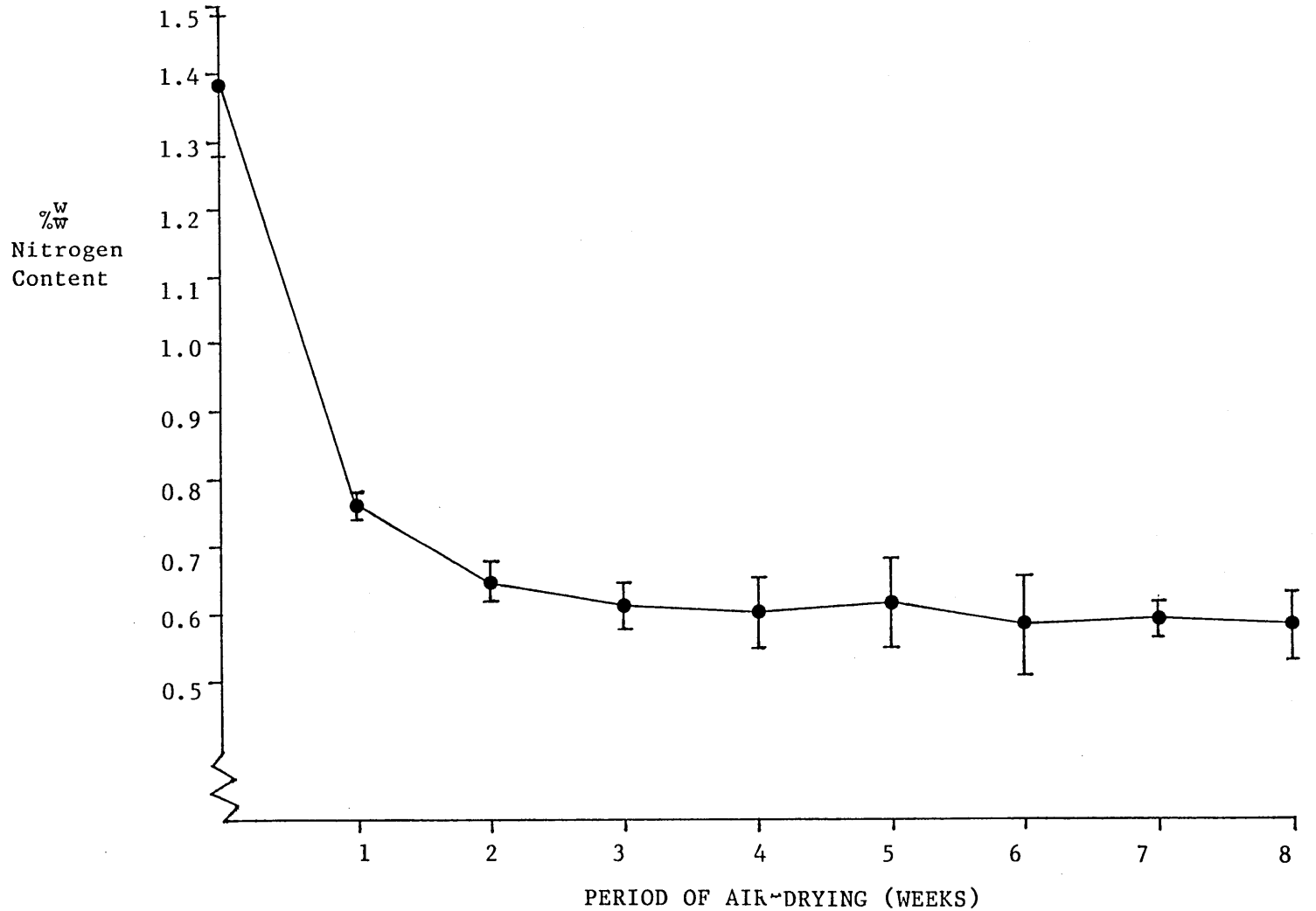
The nitrogen contents of blocks fell rapidly during the first two weeks of air-drying in the fan oven but stabilised after four weeks, showing only a very gradual fall after this time.

Table 3.8

Mean % $\frac{w}{w}$ nitrogen contents (± standard deviations) of 0.566% $\frac{w}{v}$ ACA treated lime blocks during air-drying at 25°C in a fan oven

Period of air-drying (Weeks)	% $\frac{w}{w}$ Nitrogen Content
0	1.384 ± 0.054
1	0.765 ± 0.017
2	0.651 ± 0.032
3	0.617 ± 0.034
4	0.602 ± 0.053
5	0.620 ± 0.065
6	0.582 ± 0.074
7	0.594 ± 0.026
8	0.583 ± 0.051

FIG 3.3 NITROGEN CONTENTS ($\pm$)STANDARD DEVIATIONS) OF 0.566%$^{w}_{v}$ ACA TREATED LIME BLOCKS DURING AIR-DRYING AT 25°C



Conclusion

The initial large fall in nitrogen contents of the wood blocks during the first two weeks of air-drying represents a loss of volatile aqueous ammonia from the blocks as they dried. This loss of volatile ammonia seemed to be complete after four weeks of air-drying since subsequent losses of nitrogen from the blocks were very small.

However, after four weeks of air-drying, the wood blocks still contained considerably more nitrogen than untreated lime centre wood (about 0.5% $\frac{w}{w}$ nitrogen instead of the usual 0.12 to 0.15% $\frac{w}{w}$ nitrogen in untreated lime centre). This residual extra nitrogen present in ACA treated lime after air-drying is probably either in the form of ammonium ions complexed to cation exchange sites on the wood or in the form of ammonium salts. The continued very gradual loss of nitrogen from wood blocks after four weeks of air-drying may represent the gradual volatilisation of ammonia from ammonium salts.

Standard drying procedure

A standard air-drying procedure was adopted for all subsequent experiments on ACA treated wood to ensure that all volatile aqueous ammonia had been lost from the wood blocks and that the blocks had therefore reached a stable nitrogen content. All ACA treated wood blocks were air-dried for five weeks in a fan oven at 25°C.

3.2.3.2 Determination of ammonium nitrogen in wood

General Principle

The method is a modification of a standard ammonia analysis using concentrated sodium hydroxide to release ammonia from wood

$$Na^+ + OH^- + NH_4^+ \longrightarrow Na^+ + H_2O + NH_3(g)$$

Wood samples were cut into small sticks and steam distilled in a concentrated solution of sodium hydroxide. The released ammonia was collected in boric acid solution and titrated with standard 0.01M HCl.

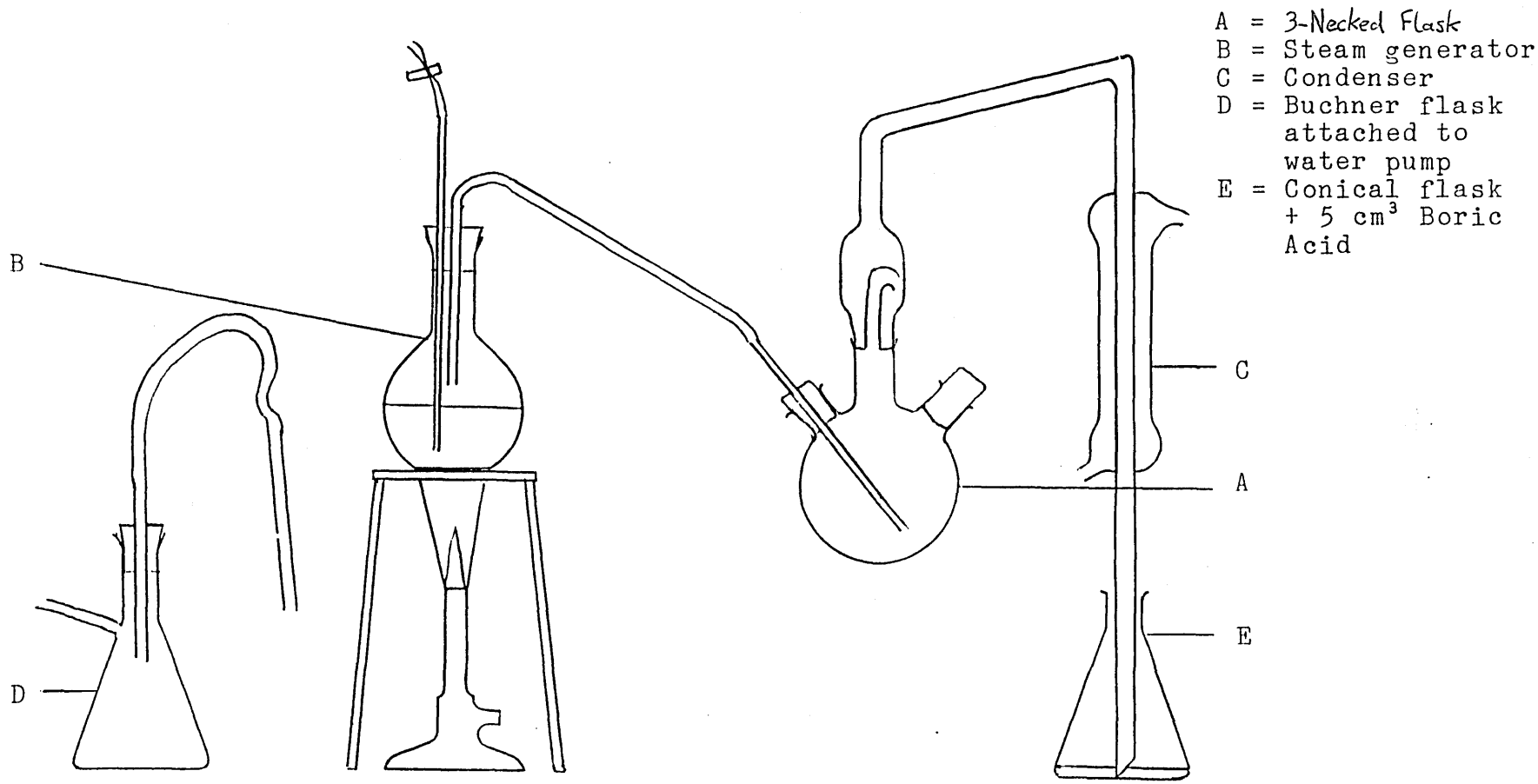
The distillation apparatus used is shown in Fig 3.4.

Analysis procedure

The apparatus was steamed using steam generator (B) for at least ten minutes prior to use and washed thoroughly with distilled water. Steam was then passed continuously through the apparatus throughout the analysis of wood blocks.

Wood blocks (weighing approximately 0.25 g), chopped into small sticks with a sharp scalpel, were placed individually into the three-necked flask (A). 10 cm^3 of 40% $\frac{W}{V}$ NaOH solution were added and the wood chips were immediately washed to the bottom of the flask

Fig 3.4 Distillation apparatus for determination of ammonium nitrogen in wood



with distilled water and the flask sealed with a stopper. The distillate was collected in a 100 cm^3 conical flask (E) containing 5 cm^3 of 2% $\frac{W}{V}$ boric acid solution and 5 drops of Kjeldahl indicator. Approximately 30 mls of distillate was collected. The ammonia collected was titrated against standard 0.01M HCl.

After each distillation, flask A was emptied by means of a vacuum produced by a water pump connected to a Buchner flask. Flask A was then rinsed with distilled water and emptied again prior to the next analysis.

3.2.3.3 Effect of NaOH concentration on the analysis procedure for determining ammonium nitrogen

Method

Sixteen centre wood blocks of pine impregnated with a 0.283% $\frac{W}{V}$ ACA solution were cured and dried according to the "standard" procedure.

Eight of the wood blocks were analysed for ammonium nitrogen by the above procedure.

The remaining eight blocks were analysed using the same procedure with the modification that a large excess of solid NaOH pellets was employed. The pellets were added to flask A at the same time as the standard volume of NaOH solution in order to maintain a high concentration of NaOH around the wood during the distillation.

Results

The means and standard deviations for the ammonium nitrogen analysis of wood blocks by the two procedures are shown in Table 3.9.

The results obtained for the two procedures were almost identical, both in terms of mean values and their standard deviations.

Table 3.9

Mean ammonium nitrogen contents of 0.283% $\frac{w}{v}$ ACA treated pine blocks (± standard deviations) by the standard analysis procedure and by a modified procedure using excess solid NaOH

	Standard Analysis Procedure	Standard Procedure + Excess solid NaOH
Ammonium nitrogen content (% $\frac{w}{w}$)	0.107 ± 0.006	0.105 ± 0.004

Conclusion

The standard analysis procedure detected a considerable quantity of nitrogen in the form of ammonia and since the modified procedure with excess solid NaOH did not

produce a higher ammonium nitrogen analysis figure, it was considered that the standard procedure had detected all available ammonium nitrogen present in the wood. The standard analysis procedure was therefore adopted for all subsequent analyses of wood blocks for ammonium nitrogen content.

3.2.3.4 The contribution of amino acids in wood to the ammonium nitrogen analysis procedure

The amino acids consistently detected in wood in significant quantities at this laboratory are arginine, aspartic acid and phenylalanine (Nayagam, *pers comm*).

It was estimated that a 10 mm x 10 mm x 5 mm lime block (weighing about 0.25 g), containing redistributed soluble nutrients, might contain a maximum of 3 milligrams of amino acid in total. Therefore, 2 cm^3 aliquots of 1.5 mg/cm^3 solutions of each of arginine, aspartic acid and phenylalanine, containing 3 mg of amino acid, were analysed for ammonium nitrogen by the standard procedure (Section 3.2.3.2).

Method

0.15 g of each of arginine, aspartic acid and phenylalanine was dissolved in distilled water and made up to 100 cm^3 in a separate flask. 2 cm^3 aliquots of each solution (containing 3 mg of amino acid) were then analysed for ammonium nitrogen content in the same manner as wood blocks. Five replicate analyses were undertaken for each amino acid.

Results

The titre values for each analysis were used to calculate µg ammonium nitrogen released during the analysis of each amino acid. The mean µg ammonium nitrogen (± standard deviations) produced by 3 mg of each of the three amino acids are shown in Table 3.10.

Table 3.10

Mean quantity (in µg) of ammonium nitrogen (± standard deviation) released during ammonium nitrogen analysis of 3 mg of arginine, asparatic acid and phenylalanine

Amino Acid	Quantity of ammonium nitrogen released (µg)($\pm \sigma^{n-1}$)
Arginine	20.58 ± 1.68
Aspartic Acid	0.42 ± 0.84
Phenylalanine	0 ± 0

Conclusions

Only arginine, with three amine groups per molecule, released significant quantities of ammonium nitrogen during the analysis procedure. 3 mg arginine released 20.58 µg of ammonium nitrogen. Therefore 3 mg arginine present in a wood block weighing 0.25 g might contribute 0.008% $\frac{w}{w}$ nitrogen to the total ammonium nitrogen analysis of the block. This figure of 0.008% $\frac{w}{w}$ nitrogen would be a maximum figure for a wood block containing surface nutrients, assuming that all amino acid was in the form of arginine. Therefore, for centre wood blocks, as used in all ACA experiments, the actual contribution of amino acids to the ammonium nitrogen analysis would be much less than 0.008% $\frac{w}{w}$ nitrogen and would not significantly affect the ammonium nitrogen figure.

3.2.3.5 Method for the determination of nitrogen copper and ammonium nitrogen contents of individual wood blocks

General procedure

Each block was cut with a sharp scalpel to produce small, thin sticks. The sticks produced from each individual block were then mixed and separated into two approximately equal portions which were weighed separately. One portion of each block was analysed for ammonium nitrogen

content (Section 3.2.3.2). The second portion was analysed for total nitrogen and copper contents (Chapter 2, Section 2.2.7).

The ammonium nitrogen, total nitrogen and copper contents were expressed in each case as a % $\frac{w}{w}$ of the pre-treatment dry mass of each block.

Test of reproducibility of procedure

Method

10 lime centre blocks were impregnated with 0.142% $\frac{w}{v}$ ACA solution, cured and air-dried according to the standard procedure (Sections 3.2.1.4 and 3.2.3.1).

The individual blocks were cut up and divided into two weighed portions as described above. Both portions of five of the blocks were analysed for % $\frac{w}{w}$ ammonium nitrogen content (Section 3.2.3.2) and both portions of the other five blocks were analysed for % $\frac{w}{w}$ nitrogen and copper (Chapter 2, Section 2.2.7). The analysis figures obtained from the two portions of each block were then compared.

Results

The ammonium nitrogen, total nitrogen and copper contents of individual block portions are shown in Table 3.11. The analyses for the two portions of each block are in adjacent columns.

Table 3.11

Ammonium nitrogen, total nitrogen and copper concentrations of individual portions of 0.142% $\frac{W}{v}$ ACA treated lime blocks

Analysis for	Block No.	Analysis figure ($\%\frac{W}{W}$)	
		Portion A	Portion B
$\%\frac{W}{W}$ Ammonium Nitrogen	1	0.129	0.123
	2	0.136	0.134
	3	0.118	0.125
	4	0.124	0.122
	5	0.119	0.116
$\%\frac{W}{W}$ Total Nitrogen	6	0.402	0.380
	7	0.348	0.365
	8	0.443	0.422
	9	0.407	0.430
	10	0.385	0.399
$\%\frac{W}{W}$ Copper	6	0.174	0.164
	7	0.140	0.150
	8	0.180	0.173
	9	0.175	0.181
	10	0.146	0.139

The results for ammonium nitrogen, total nitrogen and copper contents of blocks were analysed statistically: a paired-comparisons t-test (Sokal and Rohlf, 1973) was used to detect significant differences between the analysis figures for the two portions of the blocks.

The t values calculated for the analyses were:

$\%\frac{W}{W}$ ammonium nitrogen $t = 0.5512$

$\%\frac{W}{W}$ total nitrogen $t = -0.225$

$\%\frac{W}{W}$ copper $t = 0.3993$

For 4 degrees of freedom, none of these values are significant at the 5% probability level and there therefore is no significant difference between the analysis figures obtained for the two portions of each block.

Conclusions

The statistical analysis of the data showed no significant differences between the analysis figures for the two portions of each block for ammonium nitrogen, total nitrogen or copper contents. It was therefore concluded that analysis of one portion of a block for $\% \frac{W}{W}$ ammonium nitrogen or $\% \frac{W}{W}$ total nitrogen and copper gave a figure for each analysis which was representative of the whole block. Therefore, in subsequent experiments requiring ammonium nitrogen, total nitrogen and copper analysis, blocks were split into two portions which were analysed separately for ammonium nitrogen or total nitrogen and copper as described above.

3.2.3.6 Experiment to determine selective absorption ratios for toxic elements in ACA treated wood

Method

Five centre wood blocks of pine were impregnated with each of 0.028, 0.085, 0.142 and 0.283% $\frac{W}{V}$ ACA solutions. Five centre wood lime blocks were impregnated with each

of 0.028, 0.071, 0.142, 0.283 and 0.425% $\frac{W}{V}$ ACA solutions. The blocks were soaked in the preservative solutions for 30 minutes, patted with tissue paper and weighed wet.

After impregnation, the blocks were allowed to air-dry in the laboratory for two weeks.

The blocks were digested in A.R. concentrated H_2SO_4 and "100 volume" H_2O_2 (Chapter 2, Section 2.2.7.1). The digests were diluted and analysed for % $\frac{W}{W}$ copper and arsenic using a standard additions technique on an AAS (Chapter 2, Section 2.2.7.3).

Results

Arsenic concentrations in blocks were too low to be detected by A.A.S. analysis. Therefore, only copper results are presented.

Copper concentrations for each block were calculated from both analytical and preservative uptake data. The selective absorption ratio was then calculated for each ACA treating concentration.

Table 3.12 shows mean copper concentrations (± standard deviations) calculated from analytical and preservative uptake data for lime and pine blocks at all ACA treating concentrations. The final column of the table shows selective absorption ratios.

Table 3.12

Mean copper concentrations (± standard deviations) calculated from analytical and preservative uptake data and selective absorption ratios for ACA treated lime and pine centre blocks

Wood Type	ACA Treating Concentration (% $\frac{w}{v}$)	Analytical % $\frac{w}{w}$ Copper	Preservative Uptake % $\frac{w}{w}$ Copper	Selective Absorption Ratios
Lime	0.028	0.048 ± 0.005	0.015 ± 0.001	3.22
	0.071	0.110 ± 0.007	0.038 ± 0.003	2.88
	0.142	0.162 ± 0.012	0.077 ± 0.004	2.11
	0.283	0.280 ± 0.015	0.148 ± 0.006	1.89
	0.425	0.360 ± 0.025	0.224 ± 0.007	1.61
Pine	0.028	0.064 ± 0.006	0.014 ± 0.001	4.66
	0.085	0.147 ± 0.015	0.046 ± 0.005	3.18
	0.142	0.164 ± 0.007	0.076 ± 0.008	2.17
	0.283	0.269 ± 0.021	0.152 ± 0.011	1.77

For all blocks mean analytical % $\frac{w}{w}$ copper concentrations exceeded mean values calculated from preservative uptake data. Selective absorption ratios of copper for both wood types decreased with increasing ACA treating concentration. Selective absorption ratios fell from 3.22 for 0.028% $\frac{w}{v}$ ACA to 1.61 for 0.425% $\frac{w}{v}$ ACA in lime and from 4.66 for 0.028% $\frac{w}{v}$ ACA to 1.77 for 0.283% $\frac{w}{v}$ ACA in pine.

Conclusions

The pattern of decreasing selective absorption ratio of copper with increasing treating concentration for both lime and pine when using ACA is similar to that observed when using CCA (Chapter 2, Table 2.7). However, the ratios of copper are considerably higher in ACA treated wood than in CCA treated wood.

3.2.3.7 Leaching study on ACA treated wood

This study was undertaken to determine the effect of aqueous leaching on the concentrations of ammonium nitrogen, total nitrogen, copper and arsenic in ACA and ammonia treated wood.

Method

Lime, pine and spruce centre wood blocks treated with a range of ACA concentrations or a 1.35% $\frac{w}{v}$ ammonia solution

were subjected to a 6 day aqueous leaching programme.

Table 3.13 summarises the impregnation of blocks and the number of replicate leached blocks and unleached controls.

Table 3.13

Number of replicate leached and unleached control lime, pine and spruce blocks treated with each concentration of ACA or with ammonia solution

Treating Solution	Number of Replicate Blocks					
	Lime		Pine		Spruce	
	Unleached Controls	Leached	Unleached Controls	Leached	Unleached Controls	Leached
1.35% $\frac{w}{v}$ NH_3	6	6	5	4	5	4
0.012% $\frac{w}{v}$ ACA	-	-	5	4	5	4
0.028% $\frac{w}{v}$ ACA	6	6	5	4	5	4
0.071% $\frac{w}{v}$ ACA	6	6	5	4	5	4
0.142% $\frac{w}{v}$ ACA	6	6	5	4	5	4
0.283% $\frac{w}{v}$ ACA	6	6	-	-	-	-

All blocks were impregnated, cured and air-dried according to the "standard" procedure (Sections 3.2.1.4 and 3.2.3.1).

Leaching of wood blocks

This is an adaptation of the leaching procedure used for CCA treated blocks (Section 3.2.2.1). Blocks were

leached at 25 ± 1°C in groups of 10 in 400 cm^3 of distilled water in 1 litre beakers on magnetic stirrers for 6 days. The water was changed daily.

Analysis of blocks

All blocks were split into two weighed portions, one of which was analysed for % $\frac{w}{w}$ ammonium nitrogen and the other was anlysed for % $\frac{w}{w}$ total nitrogen copper and arsenic (Section 3.2.3.5). However, the arsenic concentrations in the blocks were too low to be detected by the A.A.S. analysis procedure and therefore arsenic concentrations were not determined.

6 untreated control blocks of each wood type were also analysed for ammonium nitrogen, total nitrogen and copper contents as described above.

Results

Mean ammonium nitrogen, total nitrogen and copper concentrations of all leached and unleached ammonia and ACA treated blocks (± standard deviations) are shown in Table 3.14. Corresponding values for unleached, untreated control blocks are shown in Table 3.15.

Table 3.14

Mean % $\frac{W}{W}$ ammonium nitrogen, total nitrogen and copper concentrations (± standard deviations) for leached and unleached ammonia and ACA treated lime, pine and spruce blocks

Wood Type	Treating Solution	% $\frac{W}{W}$ Ammonium Nitrogen		% $\frac{W}{W}$ Total Nitrogen		% $\frac{W}{W}$ Copper	
		Un-Leached	Leached	Un-Leached	Leached	Un-Leached	Leached
Lime	1.35% $\frac{W}{V}$ NH_3	0.114± 0.005	0.047± 0.001	0.358± 0.027	0.260± 0.010	0.015± 0.001	0.020± 0.001
	0.028% $\frac{W}{V}$ ACA	0.128± 0.001	0.050± 0.001	0.373± 0.049	0.247± 0.030	0.048± 0.004	0.051± 0.010
	0.071% $\frac{W}{V}$ ACA	0.130± 0.004	0.053± 0.004	0.373± 0.060	0.256± 0.031	0.108± 0.014	0.088± 0.014
	0.142% $\frac{W}{V}$ ACA	0.128± 0.008	0.046± 0.002	0.413± 0.059	0.264± 0.040	0.161± 0.019	0.126± 0.014
	0.283% $\frac{W}{V}$ ACA	0.147± 0.018	0.054± 0.002	0.438± 0.023	0.304± 0.053	0.286± 0.039	0.245± 0.038
Pine	1.35% $\frac{W}{V}$ NH_3	0.096± 0.008	0.038± 0.002	0.224± 0.003	0.159± 0.021	0.006± 0.002	0.010± 0.001
	0.012% $\frac{W}{V}$ ACA	0.103± 0.017	0.039± 0.006	0.259± 0.023	0.164± 0.009	0.035± 0.009	0.027± 0.008
	0.028% $\frac{W}{V}$ ACA	0.110± 0.004	0.041± 0.003	0.283± 0.017	0.182± 0.013	0.050± 0.004	0.047± 0.005
	0.071% $\frac{W}{V}$ ACA	0.113± 0.004	0.041± 0.002	0.300± 0.030	0.191± 0.024	0.098± 0.007	0.079± 0.012
	0.142% $\frac{W}{V}$ ACA	0.111± 0.004	0.047± 0.002	0.332± 0.017	0.205± 0.018	0.147± 0.013	0.115± 0.015
Spruce	1.35% $\frac{W}{V}$ NH_3	0.092± 0.020	0.035± 0.001	0.227± 0.015	0.164± 0.014	0.015± 0.002	0.016± 0.001
	0.012% $\frac{W}{V}$ ACA	0.095± 0.005	0.039± 0.007	0.266± 0.012	0.159± 0.018	0.038± 0.006	0.027± 0.004
	0.028% $\frac{W}{V}$ ACA	0.107± 0.015	0.043± 0.004	0.315± 0.034	0.173± 0.019	0.069± 0.017	0.056± 0.012
	0.071% $\frac{W}{V}$ ACA	0.115± 0.003	0.040± 0.003	0.317± 0.018	0.198± 0.022	0.105± 0.014	0.081± 0.015
	0.142% $\frac{W}{V}$ ACA	0.127± 0.025	0.043± 0.005	0.351± 0.021	0.201± 0.030	0.156± 0.011	0.127± 0.017

Table 3.15

Mean % $\frac{w}{w}$ ammonium nitrogen, total nitrogen and copper concentrations (± standard deviations) for unleached, untreated lime, pine and spruce blocks

Wood Type	% $\frac{w}{w}$ Ammonium Nitrogen	% $\frac{w}{w}$ Total Nitrogen	% $\frac{w}{w}$ Copper
Lime	0.025 ± 0.003	0.155 ± 0.032	0.015 ± 0.002
Pine	0.019 ± 0.001	0.080 ± 0.005	0.009 ± 0.002
Spruce	0.021 ± 0.002	0.124 ± 0.008	0.015 ± 0.001

Ammonium nitrogen and total nitrogen data

Comparison of ammonium nitrogen and total nitrogen contents of unleached ammonia and ACA treated blocks (Table 3.14) with the corresponding data for untreated blocks (Table 3.15) shows that treatment of both a hardwood and softwoods with ammonia or ACA solution increased the ammonium nitrogen and total nitrogen contents considerably.

Both ammonium and total nitrogen contents were higher in unleached ACA treated blocks than in unleached blocks treated with ammonia alone and ammonium and total nitrogen concentrations increased with increasing ACA treating concentration. However, these increases in ammonium and total nitrogen contents with increasing ACA treating concentration were small compared with the large increases in copper concentration: in unleached lime blocks, the ammonium and total nitrogen contents respectively rose from

0.128 to 0.147% $\frac{W}{W}$ and from 0.373 to 0.438% $\frac{W}{W}$ as the ACA treating concentration was increased from 0.028% $\frac{W}{V}$ to 0.283% $\frac{W}{V}$ whereas the copper concentration increased from 0.048 to 0.286% $\frac{W}{W}$. A similar pattern was observed for pine and spruce. Therefore, as the ACA treating concentration was increased, the ratio of copper to nitrogen also increased.

Comparison of ammonium nitrogen data with total nitrogen data for unleached ammonia treated, ACA treated and untreated blocks shows that only part of the increase in total nitrogen concentration observed in blocks as a result of ammonia or ACA treatment can be accounted for by an increase in ammonium nitrogen content: increases in ammonium nitrogen content during ammonia or ACA treatment rarely exceeded 0.100% $\frac{W}{W}$ nitrogen whereas increases in total nitrogen content generally exceeded 0.200% $\frac{W}{W}$ nitrogen. Therefore, for both ammonia and ACA treated blocks, less than half of the increase in total nitrogen content as a result of treatment could be accounted for by the presence of ammonium nitrogen.

Aqueous leaching of ammonia and ACA treated blocks reduced both ammonium nitrogen and total nitrogen contents considerably. At each treating concentration, the loss of total % $\frac{W}{W}$ nitrogen exceeded the loss of % $\frac{W}{W}$ ammonium nitrogen. However, despite these losses, both ammonium

nitrogen and total nitrogen contents of the leached ammonia and ACA treated blocks were still considerably higher than the corresponding values for unleached untreated wood.

After leaching, both ammonium nitrogen and total nitrogen contents were still higher in ACA treated blocks than in ammonia treated blocks, as was the case with the unleached blocks and ammonium nitrogen and total nitrogen contents still increased with increasing ACA treating concentration.

Copper data

Copper contents of unleached ACA treated lime and pine blocks (Table 3.14) were broadly similar to those of lime and pine blocks treated with the same ACA treating concentrations in the previous experiment (Table 3.12). Copper contents in unleached ACA treated spruce blocks slightly exceeded those of pine blocks treated with the same concentration of ACA.

Selective absorption ratios, calculated as described previously (Section 3.2.3.6) are shown in Table 3.16. The ratios for ACA treated lime and pine blocks were similar to those found in the previous experiment. Ratios for spruce were similar to those of pine blocks treated with the same concentration of ACA.

Table 3.16

Selective absorption ratios of copper for ACA treated lime, pine and spruce blocks

ACA Treating Concentration	Wood Type		
	Lime	Pine	Spruce
0.012% $\frac{w}{v}$	-	7.00	5.43
0.028% $\frac{w}{v}$	3.20	3.85	4.06
0.071% $\frac{w}{v}$	3.18	3.06	2.50
0.142% $\frac{w}{v}$	2.37	2.07	1.77
0.283% $\frac{w}{v}$	2.09	-	-

Table 3.17

Percentage loss of copper from ACA treated lime, pine and spruce blocks during aqueous leaching

ACA Treating Concentration	Wood Type		
	Lime	Pine	Spruce
0.012% $\frac{w}{v}$	-	22.86	28.95
0.028% $\frac{w}{v}$	0	16.00	18.84
0.071% $\frac{w}{v}$	18.52	19.39	22.86
0.142% $\frac{w}{v}$	21.74	21.77	18.59
0.283% $\frac{w}{v}$	14.34	-	-

Leached ACA treated blocks generally contained lower concentrations of copper than their unleached counterparts (Table 3.8): only lime blocks treated with 0.028% $\frac{W}{v}$ ACA did not show loss of copper during leaching. Percentage losses of copper, calculated from the mean analytical copper values for leached and unleached blocks are shown in Table 3.17. Percentage losses of copper were similar in all wood types and at all ACA treating concentrations, being approximately 20% in most cases.

3.2.3.8 The effect of ammonia concentration in an ACA solution on the nitrogen content of treated wood

Method

Treating solutions

From the 1.42% $\frac{W}{v}$ stock ACA solution, four 0.283% $\frac{W}{v}$ ACA solutions were prepared containing approximately 0.27, 1.0, 2.0 and 3.0% $\frac{W}{v}$ ammonia. 100 cm^3 aliquots of 1.42% $\frac{W}{v}$ ACA solution were pipetted into each of four 500 cm^3 volumetric flasks. Using a measuring cylinder, 13.5, 32 and 50.5 cm^3 of 0.880 ammonia solution were added to three of the flasks and all four flasks were made up to the mark with distilled water. The solutions were checked for copper and nitrogen contents (Section 3.2.1.3).

Impregnation and curing

Fifteen lime and fifteen pine centre blocks were treated with each of the four preservative solutions, cured and dried following the established procedure (Section 3.2.3.1).

Experimental procedure

After air-drying, five blocks of each wood type treated with each preservative solution were dried in an oven at 102 ± 2°C for 3 hours. A further five blocks of each type were leached in distilled water for 6 days. The blocks were leached in their groups of 5 in 200 cm^3 of distilled water in 1 litre beakers on magnetic stirrers (Section 3.2.2.1). The water was changed daily.

All wood blocks were digested and analysed individually for nitrogen content by a micro-Kjeldahl technique (Chapter 2, Section 2.2.7.2).

Results

Mean % $\frac{W}{W}$ nitrogen contents (± standard deviations) of control, oven-dried and aqueous leached lime and pine blocks treated with each preservative solution are shown in Table 3.18.

Table 3.18

Mean % $\frac{W}{W}$ nitrogen contents (± standard deviations) for control, oven-dried and aqueous leached lime and pine blocks treated with 0.283% $\frac{W}{V}$ ACA solutions containing different concentrations of ammonia

Treating Solution	Wood Type					
	Lime			Pine		
	Control	Oven-Dried	Leached	Control	Oven-Dried	Leached
0.283% $\frac{W}{V}$ ACA +0.27% $\frac{W}{V}$ NH_3	0.320 ± 0.032	0.196 ± 0.010	0.190 ± 0.019	0.315 ± 0.018	0.167 ± 0.015	0.156 ± 0.016
0.283% $\frac{W}{V}$ ACA +1.0% $\frac{W}{V}$ NH_3	0.560 ± 0.087	0.265 ± 0.021	0.271 ± 0.027	0.531 ± 0.076	0.213 ± 0.027	0.200 ± 0.031
0.283% $\frac{W}{V}$ ACA +2.0% $\frac{W}{V}$ NH_3	0.835 ± 0.126	0.349 ± 0.015	0.346 ± 0.054	0.752 ± 0.093	0.291 ± 0.064	0.293 ± 0.015
0.283% $\frac{W}{V}$ ACA +3.0% $\frac{W}{V}$ NH_3	1.031 ± 0.074	0.394 ± 0.020	0.379 ± 0.055	0.887 ± 0.097	0.345 ± 0.041	0.332 ± 0.043

The mean nitrogen data for control blocks show that, for both lime and pine blocks, as the concentration of ammonia in the ACA treating solution increased, the nitrogen content of the wood blocks after five weeks of air-drying at 25°C also increased. Nitrogen contents of lime and pine blocks increased from 0.320 to 1.031% $\frac{W}{W}$ and from 0.315 to 0.887 respectively as the ammonia concentration in the ACA treating solution was increased from 0.27% $\frac{W}{V}$ to 3.00% $\frac{W}{V}$.

Both oven-drying at 102°C and aqueous leaching considerably reduced the nitrogen contents of lime and pine blocks treated with all preservative solutions and oven-dried and leached blocks which had been treated with the same concentration of ammonia in the ACA treating solution had similar final nitrogen contents. However, as the ammonia concentration in the ACA solution increased, the final nitrogen content of both oven-dried and leached blocks also increased. Nitrogen contents of oven-dried and leached lime and pine blocks increased from about 0.19 to 0.39% $\frac{W}{W}$ nitrogen and from about 0.16 to 0.34% $\frac{W}{W}$ nitrogen respectively as the ammonia concentration in the ACA treating solution rose from 0.27 to 3.00% $\frac{W}{V}$.

3.2.3.9 Determination of the pH of ACA treated wood

Method

Fifteen centre wood blocks of lime and fifteen centre wood blocks of pine were treated with each of a 0.142% $\frac{W}{V}$ and a 0.566% $\frac{W}{V}$ ACA solution, cured wet for two weeks and air-dried for five weeks according to the standard procedure (Section 3.2.3.1). Fifteen untreated centre wood blocks of both lime and pine were also prepared.

The pH of the blocks was determined using an adaptation of the method of Gray (1968). Blocks were converted to wood flour in a hammer mill fitted with a 40 mesh sieve. Wood flour produced from all fifteen blocks of each wood

type at each treating concentration was added together, mixed and divided into three portions, each weighing approximately 1 g. Each portion of wood flour was then mixed with 3 cm^3 of distilled water in a separate test-tube and allowed to stand for 1 hour. The pH of the moistened wood flour was then determined using a calibrated pH meter.

Results

The mean pH values for untreated and ACA treated lime and pine blocks are shown in Table 3.19. Each value is the mean of three readings.

Table 3.19

Mean pH values for untreated and ACA treated lime and pine blocks

Treating Solution	pH Value	
	Lime	Pine
Untreated	4.50	4.42
0.142% $\frac{W}{V}$ ACA	5.55	5.70
0.566% $\frac{W}{V}$ ACA	5.68	5.95

The pH of both lime and pine was increased considerably by treatment with ACA, despite the five week air-drying period after curing. The pH was slightly higher in blocks treated with the 0.566% $\frac{W}{V}$ ACA solution than in those treated with the lower concentration of 0.142% $\frac{W}{V}$ ACA.

3.3 Discussion

3.3.1 Leaching studies on CCA treated wood

In terms of the aims of the studies, the following main conclusions can be drawn:

1. The inclusion of a two-week air-drying period after wet curing of 3% $\frac{W}{V}$ CCA treated lime and pine blocks did not influence the percentage losses of copper and chromium during subsequent aqueous leaching (Table 3.3).

2. During leaching studies on 3 and 5% $\frac{W}{V}$ CCA treated lime and pine blocks, neither an aqueous soil extract nor a bacterial suspension in an aqueous soil extract removed a larger percentage of preservative elements than distilled water (Table 3.7).

In addition to the above major conclusions, the following observations were made:

1. During aqueous leaching of 3 and 5% $\frac{W}{V}$ CCA treated lime and pine blocks, percentage losses of chromium (Table 3.7) were small (generally less than 3%). Percentage losses of copper ranged from 9 to nearly 13% and arsenic losses ranged from 10 to more than 14.5%. Percentage losses of copper and chromium were slightly lower from blocks treated with 5% $\frac{W}{V}$ CCA than from blocks treated with 3% $\frac{W}{V}$ CCA. Losses of copper, at a low level, continued after six days of aqueous leaching (Fig 3.1).

2. Copper, chromium and arsenic were selectively absorbed during impregnation of lime and pine blocks with 3 and 5% $\frac{w}{v}$ CCA solutions (Table 3.6). Ratios were invariably highest for arsenic and lowest for copper and the ratio for each element was lower in blocks treated with 5% $\frac{w}{v}$ CCA than in blocks treated with 3% $\frac{w}{v}$ CCA.

The percentage losses of copper and chromium from air-dried and undried 3% $\frac{w}{v}$ CCA treated lime and pine blocks (Table 3.3) show that the inclusion of a two week air-drying period after two weeks of wet curing of blocks did not influence the resistance of the preservative elements to subsequent aqueous leaching.

In the absence of moisture, chemical reactions between CCA and wood must cease. Therefore, in CCA treated blocks cured at high relative humidity for two weeks and then gradually air-dried for two weeks, according to the British Standard procedure (BS6009, 1982), fixation reactions between preservative elements and wood would be expected to be terminated during the air-drying period. Therefore, the air-drying period cannot contribute much to the fixation of the CCA to wood and leach resistance of preservative elements must be dependent on fixation reactions occurring during the two weeks of moist curing.

In CCA treated sawdust, some chemical reactions, as demonstrated by fluctuations in pH, continue for several months (Dahlgren and Hartford, 1972c). However, Henshaw (1979) found that in CCA treated wood blocks held at 20°C and 83% relative humidity after impregnation, maximum leach resistance of preservative elements was achieved after only two weeks. Therefore, any fixation reactions continuing in moist CCA treated blocks more than two weeks after impregnation apparently have no effect on the leachability of toxic elements. Therefore, providing the temperature and relative humidity are sufficient to allow completion of primary fixation reactions within two weeks, leading to maximum leach resistance of toxic elements, continued curing or air-drying of the blocks should not influence preservative leachability.

The aqueous soil extract used in the current experiment did not influence the leachability of copper, chromium and arsenic from CCA treated lime and pine blocks (Table 3.7). The pale straw-coloured extract was derived from a well cultivated alluvial loam which, although not chemically analysed, must have contained quantities of organic compounds and inorganic salts. It is therefore apparent that at the concentrations found in the soil extract, these compounds do not influence CCA stability. It has been shown (Plackett, 1984) that high concentrations of ions of calcium, magnesium and potassium in solution increase the leachability of copper from CCA treated wood, probably

as a result of competition for cation exchange sites in the wood. Therefore an aqueous soil extract derived from a well fertilised soil and containing high concentrations of these cations might have increased copper losses considerably. Thus, highly cultivated soils with a high cationic content would be expected to adversely affect the performance of CCA treated wood emplaced in them: solubilisation of copper by soil cations may partially explain the reported premature failure of CCA treated pine posts in horticultural soils in New Zealand (Butcher, 1984).

Although the aqueous soil extract used in the present studies was of virtually neutral pH (pH 6.5), an extract with a lower pH might have caused considerable solubilisation and leaching of copper from CCA treated wood blocks. Hydrogen ions may displace copper fixed to cation exchange sites in wood and highly acidic soil solutions, with a high hydrogen ion concentration, would therefore be expected to rapidly leach all exchangeable copper from CCA treated wood.

The presence of a bacterial suspension in the aqueous soil extract also failed to influence the leachability of preservative elements from CCA treated lime and pine blocks (Table 3.7). The observed solubilisation of preservative elements from CCA treated wood by fungal metabolites (Levi, 1976) may be due to acid secretions

produced by the fungi during growth. However, bacteria which are generally less tolerant of acidic conditions than fungi, may not produce secretions capable of causing preservative solubilisation. Therefore, although bacteria are primary colonisers of CCA treated wood in soil (Clubbe and Levy, 1982), their effects on the wood clearly do not include preservative solubilisation.

In both of the CCA leaching experiments, percentage losses of preservative elements were comparatively low (Tables 3.3 and 3.7). Chromium was particularly resistant to aqueous leaching with percentage losses generally being less than 3%. This element is generally highly resistant to leaching from wood treated with type C formulations of CCA (Henry and Jeroski, 1967; Wallace, 1968). The low percentage losses of chromium observed reflect the formation of highly insoluble chromium compounds or complexes in the wood: chromium may form "chromate bridges" linking four guaiacyl units in lignin (Pizzi, 1982a; b; c) and may also become complexed to the wood or precipitated in the form of $CrAsO_4$ and $Cr(OH)_3$ (Dahlgren and Hartford, 1972a; b; c).

Percentage losses of copper during aqueous leaching ranged from 9 to nearly 13% (Tables 3.3 and 3.7). This element may become fixed to wood in the form of copper chromate complexed with lignin (Pizzi, 1982a; b; c), by precipitation in the form of copper arsenates or by cation exchange mechanisms. Copper attached to cation exchange

sites in CCA treated wood should be susceptible to gradual depletion during prolonged aqueous leaching, possibly accounting for the observed continued small losses of this element after six days of aqueous leaching (Fig 3.1).

Percentage losses of arsenic, calculated using the analytical data for leached blocks and unleached controls, were less reliable than those calculated for copper and chromium. However, percentage losses of arsenic were generally higher than those of copper, regardless of wood type or CCA treating concentration. This element probably becomes fixed to wood in the form of copper (II) or chromium (III) arsenates either complexed to the wood substance or in the form of precipitates.

The selective absorption ratios of copper, chromium and arsenic in unleached control blocks (Table 3.6) generally exceeded one. Thus blocks took up more of each preservative element than would be expected from uptake of preservative solution. This phenomenon, previously observed by Smith and Williams (1973b), Henshaw (1979) and King, Smith, Baecker and Bruce (1981) probably results from adsorption, cation exchange and complexing reactions between preservative elements and the wood during impregnation. Such reactions would lead to a reduction in the concentration of the elements in solution within the

wood and a consequent diffusion of further elements into the wood from the preservative solution outside.

Although it is anionic, arsenic invariably showed a higher selective absorption ratio than either copper or chromium. Thus arsenic must react rapidly with copper and chromium, forming either complexes with wood constituents or precipitates. The selective absorption ratio was invariably lowest for copper, suggesting that during the initial reactions between CCA and wood, chromium reacts preferentially with arsenic. Thus, selective absorption of copper may result primarily from adsorption and cation exchange fixation.

3.3.2 Studies on ACA treatment and ACA treated wood

In terms of the main aims of these studies, the following conclusions can be drawn:

1. Treatment of blocks of the hardwood lime and the softwoods pine and spruce with ammonia or ACA solution increased the total nitrogen and ammonium nitrogen contents of the wood considerably (Table 3.14). The nitrogen concentration was higher in ACA treated blocks than in ammonia treated blocks and nitrogen content also increased with increasing ACA treating concentration. Although aqueous leaching removed considerable quantities of both total nitrogen and ammonium nitrogen, the total nitrogen content of leached ACA and ammonia treated blocks was still

considerably higher than that of untreated controls and also increased with increasing ACA treating concentration.

2. As the ammonia concentration in an ACA solution was increased, the nitrogen content of treated blocks of lime and pine after air-drying also increased (Table 3.18). The same pattern of increasing nitrogen content in blocks with increasing ammonia concentration in the treating solution was still observed after oven drying at 102°C for 3 hours or after 6 days of aqueous leaching.

3. Copper was selectively absorbed by lime, pine and spruce blocks during impregnation with ACA solution (Table 3.12). Selective absorption ratios of copper decreased with increasing ACA treating concentration. The selective absorption ratios for copper were considerably higher than those observed for the same element in CCA treated wood (Table 3.6).

4. During aqueous leaching of ACA treated lime, pine and spruce blocks, the copper concentration of the blocks fell. Percentage losses of copper were similar at all treating concentrations and in all wood types, amounting to about 20% of total wood copper (Table 3.17).

In addition to the main findings described above, the following conclusions can also be drawn:

1. Only part of the observed large increase in wood nitrogen content during ACA treatment could be accounted

for by an increase in the ammonium nitrogen content of the wood (Table 3.14).

2. Treatment of lime and pine blocks with ACA increased the wood pH considerably (Table 3.19).

Comparison of total nitrogen and ammonium nitrogen data for untreated controls (Table 3.15) and unleached ammonia and ACA treated blocks (Table 3.14) shows that treatment of lime, pine and spruce blocks with either ammonia or ACA solution increased both the total nitrogen and ammonium nitrogen content of the wood considerably, thus confirming the findings of Ruddick (1979). For lime blocks, treatment with ammonia solution increased the total nitrogen content to over 0.35% $\frac{W}{W}$, an increase of 0.2% $\frac{W}{W}$. Pine and spruce blocks, however, showed much smaller increases in total nitrogen content (0.144 and 0.103% $\frac{W}{W}$ respectively) following treatment with ammonia solution. The fact that the hardwood lime retained more nitrogen than the higher lignin content softwoods after ammonia treatment suggests that ammonium ions fixed to cation exchange sites in lignin do not contribute much to the total wood nitrogen content. The ammonium nitrogen contents of unleached ammonia treated lime, pine and spruce blocks were 0.114, 0.096 and 0.092% $\frac{W}{W}$ respectively whereas ammonium nitrogen contents of untreated blocks were only about 0.02% $\frac{W}{W}$ (Table 3.15).

Unleached ACA treated blocks of all three wood types invariably contained more nitrogen than ammonia treated blocks (Table 3.14) and the total nitrogen content of blocks increased with increasing ACA treating concentration. The extra nitrogen present in ACA treated blocks compared to ammonia treated blocks must represent nitrogen associated with preservative elements, possibly in the form of amine complexes with copper. However, the ammonium nitrogen content of blocks did not increase significantly with ACA treating concentration. Therefore, most of the nitrogen associated with preservative elements was not detectable as ammonium nitrogen.

Although both total nitrogen contents and ammonium nitrogen contents of wood blocks of all wood types were increased by ammonia or ACA treatment, the increase in total nitrogen content invariably considerably exceeded the increase in ammonium nitrogen content (Tables 3.14 and 3.15): in unleached lime blocks, the increase in total nitrogen content ranged from 0.2% $\frac{w}{w}$ for ammonia treated blocks to 0.28% $\frac{w}{w}$ for 0.283% $\frac{w}{v}$ ACA treated blocks whereas the increase in ammonium nitrogen content was only about 0.1% $\frac{w}{w}$ in all cases; in pine and spruce blocks the increase in total nitrogen content ranged from about 0.1% $\frac{w}{w}$ in ammonia treated spruce blocks to about 0.25% $\frac{w}{w}$ in 0.142% $\frac{w}{v}$ treated pine blocks whereas the increase in ammonium nitrogen content was generally less than 0.1% $\frac{w}{w}$.

Therefore, only part of the nitrogen added to wood blocks as a result of either ammonia or ACA treatment was detectable as ammonium nitrogen by the experimental procedure used in this study.

The ammonium nitrogen analysis procedure would be expected to displace and hence detect any exchangeable ammonium ions and ammonia complexed with copper as cuprammonium ions. However, ammonia may become associated with wood as a result of other processes which might render it more resistant to displacement by concentrated aqueous sodium hydroxide.

Two possible processes involved in the uptake of ammonia by wood were proposed by Bariska and Schuerch (1977). These authors, studying the kinetics and thermodynamics of sorption and diffusion of gaseous ammonia in wood, identified two stages in the process of ammonia plasticization of wood. The first stage involved the chemosorption of ammonia by the wood. The authors pointed out that the net heat of sorption of ammonia by wood corresponded to that for hydrogen bonding. The second stage involved the uptake of ammonia in wood by physisorption and capillary condensation. Bariska and Schuerch (op cit) also discussed the effect of water on the sorption of

ammonia by wood, pointing out that whilst the rate of sorption of gaseous ammonia by wood is faster in the presence of moisture, water can also displace ammonia previously sorbed to wood. However, it is highly doubtful whether ammonia bound to wood by either hydrogen bonding or adsorption processes would be resistant to detection by the ammonium nitrogen analysis procedure.

It is also possible that some ammonia might be converted to non-ammoniacal nitrogen, resistant to removal from the wood by the action of hot alkali. However, the mechanism of such a conversion is not clear.

Leached ammonia and ACA treated lime, pine and spruce blocks contained considerably less nitrogen and ammonium nitrogen than unleached blocks (Table 3.14). The total nitrogen contents of ammonia and ACA treated blocks of all wood types generally fell by at least 0.1% $\frac{w}{w}$ during aqueous leaching and ammonium nitrogen contents of leached blocks were generally below 0.05% $\frac{w}{w}$, representing a fall more than 0.05% $\frac{w}{w}$ in all cases. Therefore, much of the extra nitrogen present in unleached blocks following ammonia or ACA treatment was clearly water soluble and at least half of this soluble nitrogen was in the form of ammonium nitrogen.

Even after aqueous leaching, ammonia and ACA treated blocks of all wood types still contained considerably more nitrogen than untreated wood (Tables 3.14 and 3.15). The nitrogen contents of the leached blocks also increased with increasing ACA treating concentrations as for unleached blocks, showing that after aqueous leaching, some nitrogen was still associated with copper and arsenic in the wood. Ammonium nitrogen contents of leached blocks, although still double those of untreated blocks, were low (generally less than 0.05% $\frac{W}{W}$) and only accounted for one quarter to one fifth of the total wood nitrogen content.

Nitrogen analysis of lime and pine blocks treated with 0.283% $\frac{W}{V}$ ACA solutions containing varying concentrations of ammonia (Table 3.18) showed that, as the ammonia concentration in the ACA treating solution was increased, the final nitrogen content of the wood blocks after five weeks of air-drying also increased (% $\frac{W}{W}$ nitrogen contents increased from 0.320% $\frac{W}{W}$ and 0.315% $\frac{W}{W}$ respectively for lime and pine blocks treated with an ACA solution containing 0.27% $\frac{W}{V}$ ammonia to 1.031% $\frac{W}{W}$ and 0.887% $\frac{W}{W}$ respectively for lime and pine blocks treated with an ACA solution containing 3% $\frac{W}{V}$ ammonia). It is possible that for blocks treated with ACA solutions containing 2 or 3% $\frac{W}{V}$ ammonia, five weeks of air-drying was not sufficient to allow all volatile ammonia to be lost from the blocks. Both oven drying at 102°C for 3 hours and aqueous leaching

for 6 days brought about a similar, large reduction in the nitrogen contents of blocks. However, even after oven drying or aqueous leaching, the nitrogen content of the treated blocks still increased with increasing ammonia concentration in the ACA treating solution. This shows that, as the ammonia concentration in the treating solution was increased, more nitrogen was present in a stable, non-volatile, insoluble form, presumably either as non-ammoniacal nitrogen bound to wood or possibly ammonia complexed with copper and arsenic and only gradually released during oven-drying or aqueous leaching of blocks.

Lime and pine blocks impregnated with ACA solution invariably showed higher analytical $\% \frac{W}{W}$ copper concentrations than would be predicted from their uptake of preservative solution (Table 3.12). Such selective absorption of copper in ACA treated wood is similar to that observed for preservative elements in CCA treated wood (Chapter 2, Table 2.7, Chapter 3, Tables 3.2 and 3.6) and probably results from adsorption and cation exchange fixation of copper, in the form of cuprammonium ions, to wood, during impregnation. The observed fall in selective absorption ratio of copper with increasing ACA treating concentration probably results from saturation of available adsorption and cation exchange sites at higher treating concentrations.

The selective absorption ratios for copper were much higher in ACA treated wood (Table 3.12) than in CCA treated wood (Chapter 2, Table 2.7). In ACA treated wood,

copper does not have to compete with chromium ions for available adsorption and cation exchange sites on wood. In addition, the presence of ammonia in the ACA treating solution may accelerate preservative penetration of the wood, making more adsorption and cation exchange sites available for binding of copper.

Comparison of analytical copper concentrations in aqueous leached and unleached ACA treated lime, pine and spruce blocks (Table 3.14) showed that, during aqueous leaching, copper was lost from the blocks. Percentage losses of copper from blocks (Table 3.17) were about 20% in all wood types at all treating concentrations. This observation contrasts with the copper losses from CCA treated wood blocks during soil burial (Chapter 2, Table 2.6) and during aqueous leaching (Table 3.7) where the percentage loss decreased with increasing CCA treating concentration. These differences in copper losses between CCA and ACA treated wood probably reflect differences in the fixation mechanisms between the two preservatives and wood. In ACA treated wood, as the preservative treating concentration is increased, the proportion of copper fixed to the wood by cation exchange mechanisms should fall, as cation exchange sites are saturated, and thus the proportion of copper precipitated in the wood with arsenic should increase. Copper arsenates would be expected to be highly resistant to aqueous leaching compared to copper bound to wood by cation exchange mechanisms. Therefore,

percentage losses of copper from ACA treated wood during aqueous leaching would be expected to fall with increasing preservative treating concentration. The fact that this pattern of copper losses was not observed suggests that some of the copper present in ACA treated wood may be present in a form other than precipitated copper arsenates or cation exchange fixed cuprammonium or copper ions.

Treatment of both lime and pine blocks with ACA solutions considerably increased the wood pH (Table 3.19): the pH of lime and pine blocks was increased from about 4.5 for untreated wood to over 5.5 for ACA treated wood. This increase in wood pH probably results from binding of ammonium and cuprammonium ions to cation exchange sites on wood previously occupied by hydrogen ions and to the presence of soluble ammonium salts in the wood. The pH was slightly higher in lime and pine blocks treated with 0.566% $\frac{w}{v}$ ACA than in blocks treated with 0.142% $\frac{w}{v}$ ACA. Therefore, at higher ACA treating concentrations, more of the acid producing groups in the wood must have been neutralised by ammonia. This is consistent with the observed increase in wood nitrogen content with increasing ACA treating concentration.

Although the studies on ACA treated wood described in this chapter have not fully elucidated the fixation mechanism of ACA to wood, they have shown that, even after leaching of the wood, some nitrogen, apparently not in the form of ammonium nitrogen, is associated with the copper

and arsenic. High selective absorption ratios for copper in ACA treated wood have also demonstrated the importance of cation exchange and adsorption of this element onto wood during impregnation and the early stages of the fixation process. Percentage losses of copper during aqueous leaching of ACA treated wood have shown that at the treating concentrations used in this experiment, about 20% of the copper is present in the wood in a form susceptible to aqueous leaching.

Concluding summary

The leaching studies on CCA treated wood have shown that:

1. The air-drying of 3% $\frac{W}{V}$ CCA treated lime and pine blocks after wet curing did not influence the leachability of copper and chromium from the wood.

2. Neither an aqueous soil extract nor a bacterial suspension in an aqueous soil extract caused solubilisation of preservative elements from 3 and 5% $\frac{W}{V}$ CCA treated lime and pine.

The studies on ACA treatment and ACA treated wood have shown that:

1. Treatment of lime, pine and spruce with ammonia or ACA solutions increased the total nitrogen and ammonium nitrogen content of the wood considerably. However,

only part of the observed increase in wood nitrogen content could be accounted for by an increase in ammonium nitrogen content.

2. Since the nitrogen content of ACA treated blocks increased with increasing preservative treating concentration, some of the residual extra nitrogen was clearly associated with copper and arsenic.

3. Even after aqueous leaching, ammonia and ACA treated blocks of all wood types still contained considerably more nitrogen than untreated wood.

4. With increasing ammonia concentration in an ACA solution, the nitrogen content of ACA treated lime and pine blocks also increased. The same pattern of increasing nitrogen content in blocks with increasing ammonia concentration in the treating solution was still observed after oven drying at 102°C or aqueous leaching.

5. Selective absorption ratios of copper in ACA treated wood invariably exceeded one and decreased with increasing preservative treating concentration.

6. During aqueous leaching, ACA treated lime, pine and spruce blocks lost about 20% of their total copper, regardless of preservative treating concentration.

7. The pH of lime and pine was increased considerably after treatment with an ACA solution and subsequent air-drying for 5 weeks.

CHAPTER 4

SOIL BURIAL STUDIES USING ACA TREATED WOOD

4.1 Introduction

Ammoniacal copper arsenate (ACA) has shown promise as an effective wood preservative for timber in soil contact. However, large scale service trials have been restricted to the more decay resistant and refractory softwoods (Fritz, 1947; Davidson, 1977a; 1977b).

ACA is composed of a mixture of copper oxides or basic copper carbonate and arsenic pentoxide dissolved in an aqueous ammonia solution. This composition gives ACA potential advantages over CCA as a preservative for timber in soil. The ratio of copper to arsenic is considerably higher in ACA than in CCA: the atom ratios of copper to arsenic are 1 : 1.06 and 1.61 : 1 for CCA (type C, BS4072, 1974) and ACA (as used by Hulme and Butcher, 1977c) respectively. Also, since ACA contains no dichromate, an ACA solution contains about four times as much copper by weight as a CCA solution of the same total salt concentration. ACA can therefore be used to achieve high loadings of copper in wood, which Hulme and Butcher (1977c) considered might prevent soft-rot decay of susceptible hardwoods, without employing very large amounts of environmentally undesirable arsenic. In addition, the presence of ammonia in the treating solution may minimise problems of macro and microdistribution of preservative elements in the wood (Chapter 1). However,

the corrosive nature of cuprammonium solutions necessitates the use of stainless steel impregnation plant (Hulme, 1979).

Ruddick (1979) has shown that even after curing, ACA treated wood contains considerably more nitrogen than untreated wood. Air-dried ACA treated pine sapwood stakes stored indoors were found to contain between 0.36 and 0.60% $\frac{w}{w}$ nitrogen by weight, and even after two years of storage uncovered outdoors, ACA treated spruce poles contained up to 0.3% $\frac{w}{w}$ nitrogen in the surface regions. The nitrogen content of untreated wood was between 0,04 and 0.07% $\frac{w}{w}$. Nitrogen contents of air-dried, unleached ACA treated lime, pine and spruce blocks from the aqueous leaching experiment (Chapter 3, section 3.2.3.7) were up to 0.44, 0.33 and 0.35% $\frac{w}{w}$ respectively. After aqueous leaching, the nitrogen contents of the matched blocks were 0.3, 0.2 and 0.2% $\frac{w}{w}$ for lime, pine and spruce respectively, compared with 0.155, 0.080 and 0.124% $\frac{w}{w}$ nitrogen respectively for untreated wood. Therefore ACA contributes considerably to the total nitrogen content of the wood. If it is in a form available to micro-organisms, this residual extra nitrogen in ACA treated wood may act as a nutrient source to invading micro-organisms and thus lead to a stimulation of decay, acting in a similar way to the nitrogen component of concentrations of soluble nutrients in CCA treated wood (King, Smith, Baecker and Bruce, 1981; Chapter 2). Soluble ammonium compounds

leaching from ACA treated wood to soil might cause a chemostimulatory response in soil microflora, possibly leading to an increase in the rate of transfer of microbial biomass from soil to ACA treated wood.

Pure culture studies by Hulme and Butcher (1977c) showed that the toxic thresholds of copper in ACA and CCA treated hardwoods were similar. Several hardwood species were tested and all showed protection against soft-rot attack by *Chaetomium globosum* at similar copper loadings of both preservative types, although toxic thresholds varied according to wood species. However, nitrogen contents of the treated wood prior to testing were not reported.

Pure culture studies of this type may not be representative of a soil situation for ACA treated wood since any chemostimulatory effects of soluble nitrogenous compounds in the wood on micro-organisms cannot be as large in a solid agar medium as in a soil system. Leaching losses of toxic elements and soluble nitrogenous compounds from ACA treated wood would also be much greater if the wood were emplaced in soil.

Laboratory based soil burial studies similar to that described for CCA treated wood in Chapter 2 have not previously been undertaken using ACA treated wood. Such an experiment would allow the nitrogen dynamics of the decay of ACA treated wood in soil to be studied and would also

allow losses of preservative elements from wood to soil to be determined. Comparison of toxic thresholds and nitrogen data from such an ACA burial experiment with similar data from the CCA burial experiment (Chapter 2) might elucidate the effect of the extra nitrogen in ACA treated wood on the rate of decay and the nitrogen dynamics of such decay.

A large scale wood block soil burial study was therefore undertaken on ACA treated wood. The aims of this study were:

1. to determine the toxic thresholds of ACA in centre wood blocks of lime, pine and spruce,

2. to compare the performance of ACA with that of CCA when using similar loadings of copper in the wood,

3. to elucidate any effects of the additional nitrogen in wood following ACA treatment on the decay process,

4. to examine any changes in the ammonium nitrogen content of ACA treated wood during soil burial,

5. to determine the leachability of preservative elements from ACA treated wood during soil burial,

6. to examine the role of lignin in the nitrogen dynamics and decay of ACA treated pine blocks.

Aims 1 to 5 are dealt with in this chapter whilst the role of lignin (aim 6) forms part of the subject matter of Chapter 5.

In order to establish toxic thresholds of copper for ACA treated wood blocks, it was essential that percentage mass loss of wood blocks after soil burial was determined. This required that exhumed wood blocks be oven dried for three hours at 102°C. However, this drying procedure might cause a significant loss of any free ammonia remaining in the blocks. A preliminary experiment was therefore undertaken to determine the effect of oven drying at 102°C on the nitrogen and ammonium nitrogen contents of exhumed ACA treated wood blocks.

The unburied control blocks used in the main ACA soil burial experiment were the same blocks used to derive data for the ACA leaching experiment (Chapter 3). This allowed a comparison of copper losses from ACA treated wood blocks during aqueous leaching (Chapter 3) and during soil burial (the present study).

4.2 Materials and Methods

4.2.1 Preparation of wood blocks

Centre wood blocks (10 x 10 x 5 mm) with large (10 x 10 mm) radial faces were prepared from the sapwood region of oven dried planks of the species lime (*Tilia vulgaris*, Hayne), pine (*Pinus sylvestris*, L) and spruce (*Picea sitchensis*, Carr) as previously described (Chapter 2).

The blocks were labelled, dried at 102°C for three hours and weighed.

4.2.2 Preparation of ACA and ammonia solutions

A range of ACA solutions, all containing 1.35% $\frac{W}{V}$ ammonia, were prepared by diluting a 1.42% $\frac{W}{V}$ ACA stock solution with distilled water and ammonia solution (Chapter 3, section 3.2.1.2). A 1.35% $\frac{W}{V}$ ammonia solution was also prepared. The solutions were analysed for copper, arsenic and ammonia contents (section 3.2.1.3).

4.2.3 Impregnation, curing and drying of blocks

The impregnation, curing and drying procedures for ACA and ammonia treated blocks were identical to those described in Chapter 3. Blocks were soaked for 30 minutes in the preservative solution during impregnation and cured wet for two weeks in sealed petri-dishes (section 3.2.1.4). The cured blocks were subsequently air-dried

for five weeks at 25°C in a fan oven (section 3.2.3.1).

4.2.4 Preparation of soil

The soil source, type and preparation were identical to those described in Chapter 2 (section 2.2.5). The soil moisture content and water holding capacity were determined according to the method of Savory and Carey (1972).

4.2.5 Burial procedure

The procedure for burial of wood blocks in soil was identical to that described in Chapter 2.

Plastic boxes (260 mm long x 200 mm wide x 100 mm deep) were numbered, weighed and filled to a depth of 40 mm with soil.

Lime blocks, grouped according to sampling interval were placed in beakers. Pine and spruce blocks were mixed together before being similarly grouped in beakers according to sampling interval.

Lime blocks were buried separately from the softwood blocks due to the requirement of a higher soil moisture content for the softwoods. Blocks from different sampling intervals were buried in separate boxes.

Blocks were selected randomly from the beakers and placed, with radial faces in the horizontal plane, 3 cm apart on the soil surface in the boxes. A maximum of 20 blocks were placed in each box and their positions were noted on paper templates.

A further 40 mm of soil was then placed in each box, covering the blocks and the boxes were re-weighed to determine the weight of soil and blocks. The volume of water required to raise the moisture content to 80% WHC for lime blocks and 100% WHC for pine and spruce blocks was then added and the boxes were covered with loose-fitting lids and incubated at 25°C in a thermostatically controlled dark room. Boxes were weighed weekly to check soil moisture contents and water was added as necessary to maintain WHC.

At each sampling interval, blocks to be exhumed were located using the paper templates, carefully brushed free of adhering soil and weighed immediately.

The subsequent drying and chemical analysis of blocks differed according to experiment.

4.2.6 The effect of oven drying at 102°C on the ammonium nitrogen and total nitrogen contents of ACA treated wood blocks previously buried in soil

Table 4.1 shows the number of replicate lime, pine and spruce blocks impregnated with each ACA treating concentration.

Table 4.1

The numbers of replicate centre wood blocks of lime, pine and spruce treated with each concentration of ACA

Wood Type	ACA Treating Concentration (% $\frac{W}{V}$)			
	0.012	0.028	0.142	0.283
Lime	-	24	-	24
Pine	24	-	24	-
Spruce	24	-	24	-

The concentrations of ACA selected for each wood type corresponded to the lowest and highest concentrations used in the main burial experiment.

Blocks were impregnated, cured wet for 2 weeks and air-dried at 25°C for 5 weeks as described in section 4.2.1.

Soil burial of wood blocks

All of the blocks were buried randomly in soil for a period of 6 weeks and then exhumed and weighed wet as described in section 4.2.1.

Half of the blocks of each wood type at each ACA treating concentration were then oven dried at 102°C for 3 hours. The remaining blocks were allowed to air-dry in the laboratory for 2 weeks.

Chemical analysis of wood blocks

6 oven-dried and 6 air-dried blocks of each wood type at each ACA treating concentration were analysed for % $\frac{w}{w}$ nitrogen content (Chapter 2, section 2.2.7).

The remaining 6 oven-dried and 6 air-dried blocks of each type were analysed for % $\frac{w}{w}$ ammonium nitrogen (Chapter 3, section 3.2.3.2).

The results of this experiment (section 4.3.1), showed that oven drying at 102°C for 3 hours had no significant effect on the total nitrogen and ammonium nitrogen contents of the exhumed ACA treated wood blocks. Therefore, all blocks used in the main burial experiment were oven-dried at 102°C for 3 hours after exhumation to allow the calculation of mass loss and moisture content for each block.

4.2.7 Main ACA burial experimental procedure

Untreated, ammonia treated and ACA treated lime, pine and spruce centre wood blocks were buried in soil for periods of up to 18 weeks. Both aqueous leached and unleached lime blocks were included but all softwood blocks were unleached.

Table 4.2 shows the number of replicate leached and unleached blocks of each wood type prepared at each ACA treatment level and also shows numbers of untreated and ammonia treated controls.

Table 4.2

Number of replicate leached and unleached untreated, ammonia treated and ACA treated lime, pine and spruce blocks prepared

Treating Solution	Number of Blocks Prepared			
	Unleached Lime	Leached Lime	Unleached Pine	Unleached Spruce
Untreated	24	24	64	24
1.35% $\frac{W}{V}$ NH_3	24	24	20	20
0.012% $\frac{W}{V}$ ACA	-	-	20	20
0.028% $\frac{W}{V}$ ACA	24	24	20	20
0.071% $\frac{W}{V}$ ACA	24	24	20	20
0.142% $\frac{W}{V}$ ACA	24	24	60	20
0.283% $\frac{W}{V}$ ACA	24	24	-	-

All ammonia and ACA treated blocks were impregnated, cured and dried according to the standard procedures (Chapter 3, sections 3.2.1.4 and 3.2.3.1).

Leaching of blocks

Blocks were leached at 25°C in groups of 10 in 400 cm^3 of distilled water for 6 days with daily changes of water (Chapter 3, section 3.2.3.7).

The leached blocks were allowed to air-dry in the laboratory for 2 weeks.

Soil burial

Blocks were buried in soil as described in section 4.2.1 and were exhumed at sampling intervals of 6, 12 and 18 weeks. A quarter of the blocks of each wood type prepared at each treatment level (see Table 4.2) were buried for exhumation at each sampling interval. The remaining blocks were used as unburied controls.

After exhumation, all blocks were weighed wet, and then dried in an oven at 102°C for 3 hours. % mass losses and % moisture contents were then calculated for each block (Chapter 2, section 2.2.7).

Chemical analysis of wood blocks

10 untreated and 10 0.142% $\frac{w}{v}$ ACA treated pine blocks at each sampling interval (including unburied

controls) were set aside for lignin determinations (see Chapter 5).

All remaining blocks were split into two weighed portions, one of which was analysed for % $\frac{w}{w}$ ammonium nitrogen and the other for % $\frac{w}{w}$ total nitrogen, % $\frac{w}{w}$ copper and % $\frac{w}{w}$ arsenic (Chapter 3, section 3.2.3.5).

4.3 Results

4.3.1 The oven drying experiment

Mean % $\frac{W}{W}$ ammonium nitrogen and % $\frac{W}{W}$ total nitrogen contents (± standard deviations) of air-dried and oven-dried exhumed ACA treated lime, pine and spruce blocks are shown in Table 4.3.

Table 4.3

Mean % $\frac{W}{W}$ ammonium nitrogen and % $\frac{W}{W}$ total nitrogen contents (± standard deviations) of air-dried and oven-dried exhumed ACA treated lime, pine and spruce blocks

Wood Type	ACA Treating Concentration	% $\frac{W}{W}$ Ammonium Nitrogen		% $\frac{W}{W}$ Total Nitrogen	
		Air-Dried	Oven-Dried	Air-Dried	Oven-Dried
Lime	0.028% $\frac{W}{V}$	0.037±0.004	0.036±0.003	0.368±0.028	0.369±0.022
Lime	0.283% $\frac{W}{V}$	0.039±0.003	0.038±0.002	0.345±0.016	0.343±0.016
Pine	0.012% $\frac{W}{V}$	0.032±0.002	0.031±0.003	0.236±0.006	0.237±0.010
Pine	0.142% $\frac{W}{V}$	0.034±0.001	0.034±0.003	0.230±0.012	0.227±0.014
Spruce	0.012% $\frac{W}{V}$	0.027±0.004	0.026±0.003	0.227±0.017	0.231±0.015
Spruce	0.142% $\frac{W}{V}$	0.037±0.002	0.035±0.002	0.242±0.018	0.236±0.014

For each wood type at each ACA treating concentration, there was no significant difference between the air-dried and oven-dried values for either % $\frac{W}{W}$ ammonium nitrogen or % $\frac{W}{W}$ total nitrogen contents.

Conclusion

It was concluded that oven drying of exhumed ACA treated lime, pine and spruce blocks at 102°C for 3 hours did not significantly affect their % $\frac{w}{w}$ ammonium nitrogen and % $\frac{w}{w}$ total nitrogen contents.

4.3.2 Main ACA burial experiment

Mean values and standard deviations for all analyses are presented in Appendix II.

4.3.2.1 Weight loss data

Figures 4.1 and 4.2 show graphs of the mean percentage weight losses of leached and unleached lime and of the softwoods pine and spruce respectively.

Both leached and unleached lime blocks (Fig 4.1) at all treatment levels showed considerable decay during the 18 week burial period. Therefore, for lime blocks, the toxic thresholds with ACA had not been reached at the 0.283% $\frac{w}{v}$ level. There was also no induction phase prior to the onset of decay even at the highest ACA treating concentrations: decay was already well established in all cases by the 6 week sampling interval.

For both leached and unleached lime, ammonia treated and 0.028% $\frac{w}{v}$ ACA treated blocks showed higher mass losses

than untreated blocks at all sampling intervals. However, at higher ACA treating concentrations, the rate of decay was depressed.

Leached lime blocks generally showed lower weight losses than unleached lime blocks treated with the same concentration of ACA at each sampling interval.

From the weight loss data for the softwoods (Fig 4.2), the toxic thresholds of ACA were 0.142% $\frac{W}{V}$ and 0.071% $\frac{W}{V}$ for pine and spruce respectively. The rate of decay was apparently lower for spruce than for pine at all ACA treating concentrations except 0.142% $\frac{W}{V}$ where neither wood type showed any decay.

Comparison of weight loss data for untreated and ammonia treated pine and spruce blocks shows that, in contrast to lime blocks, the presence of ammonia did not stimulate decay.

The presence of ACA in pine and spruce blocks both reduced the rate of decay and increased the length of the induction phase prior to the onset of decay.

4.3.2.2 Statistical analysis of weight loss data

Comparisons of the percentage weight loss data were made between leached and unleached lime and between pine and spruce at all treatment levels using two-way analyses of variance. These comparisons were carried out using

the "Statpack" programme (R. Houchard, Western Michigan University, 1974) on a Decsystem 20 computer.

Table 4.4 shows the probability values obtained using the two-way analyses of variance to compare the weight loss data for leached and unleached lime blocks and for pine and spruce blocks at each preservative treatment level. The column headed "Time interval" shows that highly significant weight losses occurred in all wood types at all ACA treating concentrations with the exception of pine and spruce blocks treated with 0.142% $\frac{W}{V}$ ACA. The column headed "Wood type" shows that for lime blocks there were no significant differences in weight loss between leached and unleached blocks at all preservative treatment levels except the 0.283% $\frac{W}{V}$ ACA level. For the softwood blocks, there were highly significant differences in weight loss between pine and spruce at all ACA treating concentrations but not in ammonia treated and untreated wood. The "Interaction" column shows that for lime there was generally no significant difference between the rates of decay of leached and unleached blocks at each preservative treatment level. However, for the softwood blocks, there was a highly significant difference between the rates of decay of pine and spruce blocks treated with ammonia and at all ACA treating concentrations except 0.142% $\frac{W}{V}$ (where no decay occurred).

It can therefore be concluded from the statistical analysis of the weight loss data that aqueous leaching of untreated, ammonia treated and ACA treated lime blocks did not affect their rate of decay during subsequent burial in soil. It can also be concluded that ammonia treated and ACA treated spruce blocks decayed more slowly than pine blocks at each treatment level.

4.3.2.3 Ammonium nitrogen data

Figures 4.3 and 4.4 show graphs of the mean % $\frac{W}{W}$ ammonium nitrogen contents of leached and unleached lime blocks and of pine and spruce blocks respectively during soil burial.

Ammonium nitrogen data for unleached lime blocks (Fig 4.3) show that in the unburied control blocks, the % $\frac{W}{W}$ ammonium nitrogen contents were higher in ACA treated wood blocks than in blocks treated with ammonia alone. During the first 6 weeks of soil burial, the ammonium nitrogen contents of all treated unleached lime blocks fell considerably (all blocks lost between 0.075 and 0.100 % $\frac{W}{W}$ ammonium nitrogen). After the 6 week sampling interval, the ammonium nitrogen contents remained constant throughout the remainder of the 18 week burial period.

Leached lime unburied control blocks had much lower ammonium nitrogen contents than their unleached counterparts. During the first 6 weeks of soil burial, the ammonium

nitrogen contents of the leached blocks also fell but to a level similar to that found for unleached blocks at the same sampling interval.

Untreated lime unburied control blocks contained some ammonium nitrogen: unleached and leached blocks contained 0.025 and 0.010% $\frac{W}{W}$ ammonium nitrogen respectively. All leached and unleached untreated blocks buried in soil had similar ammonium nitrogen contents (about 0.020% $\frac{W}{W}$) regardless of sampling interval and this ammonium nitrogen accounted for most of that found in the buried ammonia and ACA treated blocks.

The ammonium nitrogen data for ammonia treated and ACA treated pine and spruce blocks (Fig 4.4) shows that ammonium nitrogen contents of the two wood types were similar for each treating concentration at each sampling interval. Both ammonia treated and ACA treated pine and spruce blocks showed a considerable fall (between 0.050 and 0.075% $\frac{W}{W}$) in ammonium nitrogen content during the first six weeks of burial in soil but thereafter the ammonium nitrogen content of all wood blocks remained constant. Although the ammonium nitrogen contents of unburied control pine and spruce blocks were higher at higher ACA treating concentrations (rising from about 0.09% $\frac{W}{W}$ for ammonia treated wood to about 0.12% $\frac{W}{W}$ for wood treated with 0.142% $\frac{W}{V}$ ACA), the ammonium nitrogen contents of all buried treated blocks were similar (about 0.03% $\frac{W}{W}$), regardless of treating concentration.

Untreated pine and spruce unburied control blocks had lower ammonium nitrogen contents than ammonia or ACA treated unburied controls and the ammonium nitrogen contents of untreated blocks remained constant throughout the burial period.

4.3.2.4 % $\frac{W}{W}$ Nitrogen data

Figures 4.5 and 4.6 show graphs of the mean % $\frac{W}{W}$ total nitrogen contents of leached and unleached lime blocks and of pine and spruce blocks respectively during soil burial.

Nitrogen data for unleached lime blocks (Fig 4.5) show that untreated blocks showed an initial increase in nitrogen content during the first 6 weeks of soil burial but beyond this sampling interval there was only a slight increase in nitrogen content. The nitrogen contents of unleached ammonia and 0.028% $\frac{W}{V}$ ACA treated blocks did not change significantly during soil burial and never exceeded 0.4% $\frac{W}{W}$ despite the fact that weight losses of these blocks exceeded 40% by the 18 week sampling interval. Unleached lime blocks treated with ACA concentrations of 0.071% $\frac{W}{V}$ and above showed a fall in nitrogen content during the first 6 weeks of soil burial. However, the nitrogen contents of these blocks increased again beyond 6 weeks and by the 18 week sampling interval had reached or exceeded 0.5% $\frac{W}{W}$ and were therefore much

higher than those of the untreated, ammonia treated and 0.028% $\frac{W}{V}$ ACA treated blocks even although the latter showed greater weight losses.

Comparison of nitrogen contents of unburied control leached and unleached ammonia and ACA treated lime blocks shows that nitrogen contents of leached blocks were about 0.1% $\frac{W}{W}$ lower than for unleached blocks at the same treatment level. All leached untreated, ammonia treated and ACA treated lime blocks showed an increase in nitrogen content during the first 6 weeks of soil burial with the nitrogen contents of ammonia and ACA treated blocks reaching 0.4% $\frac{W}{W}$. However only leached untreated blocks showed a continued increase in nitrogen content beyond 6 weeks. Their nitrogen contents also reached 0.4% $\frac{W}{W}$ by the end of the burial period.

Untreated pine and spruce blocks (Fig 4.6) showed continued increases in nitrogen content throughout the burial period. Ammonia treated pine and spruce blocks had a higher nitrogen content than untreated controls prior to soil burial but showed a more gradual increase in nitrogen content during soil burial, reaching a similar nitrogen level to the untreated blocks (about 0.4% $\frac{W}{W}$) at the end of the burial period. All ACA treated pine and spruce blocks showed a fall in nitrogen content during the first six weeks of soil burial. In most cases,

the nitrogen content increased again beyond 6 weeks, reaching 0.4% $\frac{w}{w}$ by the 18 week sampling interval in heavily decayed blocks, but the size of this nitrogen increase fell with increasing ACA treating concentration and pine blocks treated with 0.142% $\frac{w}{v}$ ACA showed no increase in nitrogen content at all.

4.3.2.5 Non-ammoniacal nitrogen

Since the large decrease in ammonium nitrogen content of ammonia and ACA treated blocks during the first 6 weeks of soil burial could mask any microbial inputs of nitrogen to the blocks over the same period, non-ammoniacal nitrogen contents were calculated in an attempt to detect microbial nitrogen inputs to the wood. Non-ammoniacal nitrogen contents were calculated for each wood type at each treating concentration for all sampling intervals by subtracting the mean ammonium nitrogen content from the mean total nitrogen content.

Non-ammoniacal nitrogen contents of leached and unleached lime blocks and of pine and spruce blocks are shown in Figures 4.7 and 4.8 respectively.

Untreated, ammonia treated and all ACA treated unleached lime blocks (Fig 4.7) showed increases in non-ammoniacal nitrogen content during the first six weeks of soil burial. However, beyond the six week sampling interval, the untreated, ammonia treated and 0.028% $\frac{w}{v}$ ACA

treated blocks showed no further increases despite considerable weight loss during the latter part of the burial experiment. Unleached blocks treated with higher concentrations of ACA did show continued increases in non-ammoniacal nitrogen content up to the 18 week sampling interval and consequently these blocks had much higher final nitrogen contents, even although they showed far lower weight losses than the untreated and ammonia treated blocks.

Leached untreated lime blocks (Fig 4.7) showed continued increases in non-ammoniacal nitrogen content throughout the burial. However, the ammonia treated and all ACA treated leached lime blocks only showed increases in non-ammoniacal nitrogen content up to the 6 week sampling interval. These increases were up to 0.2% $\frac{W}{W}$ and raised the non-ammoniacal content of the blocks to about 0.4% $\frac{W}{W}$ at the six week sampling interval. Beyond this sampling interval, there were no further increases, again despite considerable weight losses which continued up to 18 weeks.

Untreated, ammonia treated and 0.012% $\frac{W}{V}$ ACA treated pine and spruce blocks (Fig 4.8) showed continued increases in non-ammoniacal nitrogen content throughout the burial period. Comparison of the non-ammoniacal nitrogen data with the corresponding weight loss data for these blocks (Fig 4.2) suggests that there is a good correlation between

weight loss and non-ammoniacal nitrogen content. 0.028% $\frac{W}{V}$ ACA treated pine and spruce blocks only showed increases in non-ammoniacal nitrogen content beyond the 6 week sampling interval, corresponding with the time when decay started in these blocks. Pine and spruce blocks treated with 0.071 and 0.142% $\frac{W}{V}$ ACA showed no significant increases in non-ammoniacal nitrogen content during soil burial. These blocks also showed little or no decay.

4.3.2.6 Statistical correlation of weight loss and non-ammoniacal nitrogen data

Correlation coefficients for weight loss versus non-ammoniacal nitrogen content during soil burial were calculated for each wood type/treating solution using the Statpack computer programme (see Section 4.3.2.2). The correlation coefficients are shown in Table 4.5.

For unleached lime blocks, correlation between weight loss and non-ammoniacal nitrogen content was quite strong (greater than 0.8) for untreated blocks and for blocks treated with 0.071, 0.142 and 0.283% $\frac{W}{V}$ ACA solutions. However, ammonia treated and 0.028% $\frac{W}{V}$ ACA treated unleached lime blocks showed a poor correlation (less than 0.7) since these blocks showed no increase in non-ammoniacal nitrogen content beyond the 6 week sampling interval whilst weight loss continued.

For leached lime, only the untreated and 0.142% $\frac{W}{V}$ ACA treated blocks showed correlation coefficients greater than 0.8. The weaker correlation between weight loss and non-ammoniacal content in the remaining leached lime blocks corresponds with a lack of increase in non-ammoniacal nitrogen content in these blocks beyond the six week sampling interval, despite continued weight loss.

For pine and spruce blocks, there was generally a good correlation between weight loss and non-ammoniacal nitrogen content at all treatment levels up to 0.028% $\frac{W}{V}$ ACA. However, pine and spruce blocks treated with 0.071 and 0.142% $\frac{W}{V}$ ACA showed very low correlation coefficients since these blocks showed no significant decay.

4.3.2.7 Preservative data

Figures 4.9 and 4.10 show graphs of the mean % $\frac{W}{W}$ copper contents of leached and unleached lime blocks and of pine and spruce blocks respectively. Arsenic contents of blocks were too low to be detected by the A.A.S. and are therefore not presented.

Unleached ACA treated lime blocks (Fig 4.9) at all treating concentrations showed a fall in copper content during soil burial. Most of the copper was lost during the first 6 weeks of soil burial with any subsequent losses being small. Leached ACA treated lime blocks

generally showed much smaller falls in copper content during soil burial. However, leached lime blocks treated with 0.283% $\frac{W}{V}$ ACA did show a fall of about 0.05% $\frac{W}{W}$ copper during burial, the loss of copper being during the first 12 weeks.

ACA treated pine blocks at all treating concentrations (Fig 4.10) also showed a fall in copper content during soil burial. As with unleached lime, most of the copper losses from blocks occurred during the first 6 weeks of soil burial. Copper data for ACA treated spruce blocks were similar to those for ACA treated pine blocks although losses of copper from the spruce blocks were spread more evenly throughout the 18 week burial period.

Percentage loss of copper was calculated for all wood types at all ACA treating concentrations using the mean values of copper analyses of unburied control blocks and blocks from the 18 week sampling interval. These percentage losses are shown in Table 4.6.

For unleached ACA treated lime blocks, the percentage loss of copper during soil burial decreased with increasing ACA treating concentration (from over 50% for 0.028% $\frac{W}{V}$ ACA treated blocks to about 30% for 0.283% $\frac{W}{V}$ ACA treated blocks). However, the actual quantity of copper lost was greater from the blocks treated with higher concentrations of ACA, being about 0.025% $\frac{W}{W}$ copper for the

0.028% $\frac{W}{V}$ ACA treated blocks and 0.085% $\frac{W}{W}$ copper for the 0.283% $\frac{W}{V}$ ACA treated blocks (Fig 4.9).

The leached ACA treated lime blocks showed much smaller percentage losses of copper than the unleached blocks with a similar proportion (about 20%) being lost at all ACA treating concentrations.

ACA treated pine blocks also showed much lower percentage losses of copper than unleached lime blocks with a similar percentage (about 30%) being lost at all ACA treating concentrations.

ACA treated spruce blocks showed an increase in percentage loss of copper with increasing ACA treating concentration (from 5% for the 0.012% $\frac{W}{V}$ ACA treated blocks to 37% for the 0.142% $\frac{W}{V}$ ACA treated blocks).

4.3.2.8 Statistical analysis of copper data

The analytical copper data for blocks of each wood type at each ACA treating concentration were analysed statistically using one-way analyses of variance. The analysis was undertaken using the "Statpack" computer programme previously described.

Table 4.7 shows the probability values obtained using the one-way analyses of variance to determine the significance of any changes in the copper contents of ACA treated wood blocks during soil burial. The

probability values for unleached lime blocks show that, at all ACA treating concentrations, there were highly significant losses of copper during soil burial. The pine and spruce blocks, which were also unleached, similarly showed significant losses of copper at all ACA treating concentrations. However, leached lime blocks only showed significant losses at the 0.283% $\frac{w}{v}$ ACA treatment level.

4.3.2.9 Comparison of the toxic thresholds of copper in CCA and ACA treated wood

Comparisons of the toxic thresholds of copper in CCA and ACA treated lime and pine centre blocks were made using the weight loss and copper data from the 18 week CCA burial experiment (Chapter 2) and from the 18 week present study.

Despite the use of an identical experimental procedure and soil in the CCA and ACA burial experiments, the rate of decay of untreated lime centre blocks was considerably faster in the CCA experiment: at the final (18 week) sampling interval, the percentage weight losses of untreated lime centre blocks were 57.9 and 37.9% respectively for the CCA and ACA burial experiments. The rates of decay of untreated pine centre blocks in the two experiments were almost identical: the percentage

weight losses of the untreated pine blocks at the 18 week sampling interval were 19.6 and 22.1% for the CCA and ACA burial experiments respectively.

The toxic threshold of CCA for lime centre blocks was 2.0% $\frac{W}{V}$ (Fig 2.2) and the pre-burial copper content of these blocks was 0.173% $\frac{W}{W}$. In the present study, the toxic thresholds of ACA for unleached lime centre blocks had not been reached at the highest treating concentration of 0.283% $\frac{W}{V}$ (Fig 4.1), although the pre-burial copper content of these blocks was 0.286% $\frac{W}{W}$. Therefore, the toxic threshold of copper in lime centre blocks was considerably higher in the ACA burial than in the CCA burial, despite the fact that the untreated lime blocks decayed faster in the CCA burial experiment.

The toxic threshold of CCA in pine centre blocks was 0.5% $\frac{W}{V}$ (Fig 2.3) and the pre-burial copper content of these blocks was 0.062% $\frac{W}{W}$. The toxic threshold of ACA for pine centre blocks was 0.142% $\frac{W}{V}$ (Fig 4.2) and the pre-burial copper contents of these blocks was 0.147% $\frac{W}{W}$. Therefore, the toxic threshold of copper in pine centre blocks was also considerably higher in the ACA burial experiment than in the CCA burial experiment.

4.3.2.10 Statistical comparisons of the weight loss and copper data from the CCA and ACA burial experiments

All statistical analysis described in this section was undertaken using the "Statpack" computer programme.

Two-way analyses of variance were used to compare the weight loss data from the CCA and ACA burial experiments for untreated centre blocks of both lime and pine. The comparison of weight loss data for the untreated lime centre blocks showed that the rate of decay of these blocks was significantly faster in the CCA burial experiment than in the ACA burial experiment (the rate of decay was significantly faster at the 1% level). The comparison of weight loss data for the untreated pine centre blocks showed no significant difference in the rate of decay between the CCA and ACA burial experiments.

The % $\frac{W}{W}$ pre-burial copper contents of CCA and ACA treated lime and pine centre blocks were compared by means of t-tests in order to find CCA and ACA treated blocks of similar copper content which could then be further compared for decay rate. T-tests showed no significant differences between the pre-burial copper content of lime centre blocks treated with 1.0% $\frac{W}{V}$ and 0.142% $\frac{W}{V}$ ACA, pine centre blocks treated with 0.25% $\frac{W}{V}$ ACA and 0.012% $\frac{W}{V}$ ACA and pine centre blocks treated with 0.75% $\frac{W}{V}$ CCA and 0.071% $\frac{W}{V}$ ACA.

The weight loss data from the above blocks were then compared using two-way analyses of variance to detect significant differences in the rate of decay between the wood blocks at similar copper concentrations, treated with the two preservatives.

Table 4.8 shows the probabilities of differences in the weight loss data between the CCA and ACA treated lime and pine centre blocks being due to chance. Only the interaction column, showing significance of differences in the rates of decay between CCA and ACA treated blocks, has been included. This column shows that, in all three comparisons, there were highly significant differences in the rates of decay between the CCA and ACA treated blocks.

It can therefore be concluded that in all three weight loss comparisons of CCA and ACA treated lime and pine centre (Table 4.8), blocks treated with ACA decayed at a significantly faster rate than CCA treated blocks of similar pre-burial copper content. In the case of lime centre wood, the 0.142% $\frac{W}{V}$ ACA treated blocks decayed significantly faster than the 1.0% $\frac{W}{V}$ CCA treated blocks despite the fact that untreated control lime centre blocks decayed significantly more slowly in the ACA burial experiment than in the CCA burial experiment.

4.3.2.11 Comparison of nitrogen data from the CCA and ACA burial experiments

Lime

Direct comparison of the nitrogen data for CCA treated lime centre blocks (Fig 2.2, Chapter 2) and for ACA treated unleached lime centre blocks (Fig 4.5) is complicated by the loss of ammonium nitrogen which occurred from ACA

treated blocks during the first 6 weeks of soil burial. However, various conclusions can be drawn:

1. Comparison of unburied control blocks shows that the ACA treated lime blocks contained considerably more nitrogen than CCA treated blocks prior to soil burial: the nitrogen content of ACA treated blocks was about 0.4% $\frac{W}{W}$ whereas that of CCA treated blocks was only about 0.15% $\frac{W}{W}$.

2. Comparison of the nitrogen contents of CCA and ACA treated lime blocks exhumed after 18 weeks of soil burial shows that the nitrogen content of ACA treated blocks increased with increasing preservative treating concentration whereas the nitrogen content of CCA treated blocks decreased with increasing preservative treating concentration. Therefore, at the lowest treating concentrations of the two preservatives (0.5% $\frac{W}{V}$ CCA and 0.028% $\frac{W}{V}$ ACA), the nitrogen content of the CCA treated blocks exceeded that of the ACA treated blocks after 18 weeks whereas at higher treating concentrations, the nitrogen contents of ACA treated blocks were considerably higher (above 0.5% $\frac{W}{W}$) than those of CCA treated blocks (less than 0.4% $\frac{W}{W}$). The lime centre blocks treated with 1.5 and 2.0% $\frac{W}{V}$ CCA showed less than 10% weight loss at the end of the burial period and thus their nitrogen contents did not rise far above 0.2% $\frac{W}{W}$.

Inputs of nitrogen, possibly of a microbial source, to ACA treated unleached lime blocks during soil burial can be estimated from the non-ammoniacal nitrogen data. However, losses of nitrogen from such blocks during aqueous leaching cannot be accounted for solely by losses of ammonium nitrogen (Chapter 3, Section 3.2.3.7) and therefore increases in non-ammoniacal nitrogen content (total nitrogen - ammonium nitrogen) of blocks during soil burial are likely to be underestimates of total nitrogen inputs to the blocks.

ACA treated unleached lime blocks showed larger increases in non-ammoniacal nitrogen content (Fig 4.7) with increasing preservative treating concentration: increases ranged from about 0.1% $\frac{W}{W}$ nitrogen for 0.028% $\frac{W}{V}$ ACA treated blocks to more than 0.2% $\frac{W}{W}$ nitrogen for 0.283% $\frac{W}{V}$ ACA treated blocks. These differences reflect the fact that 0.028% $\frac{W}{V}$ ACA treated blocks only showed increases in nitrogen content up to the 6 week sampling interval whereas blocks treated with higher concentrations of ACA showed continued nitrogen increases throughout the burial period.

CCA treated lime centre blocks (Fig 2.2) showed smaller increases in nitrogen content at higher treating concentrations: blocks treated with 0.5% $\frac{W}{V}$ CCA showed a nitrogen increase of nearly 0.3% $\frac{W}{W}$ whereas blocks treated with 1.5% $\frac{W}{V}$ CCA only showed a nitrogen increase of 0.065% $\frac{W}{W}$. Blocks treated with 0.5 and 1.0% $\frac{W}{V}$ CCA

showed continued increases in nitrogen content, accompanying decay, throughout the burial period. However, blocks treated with 1.5 and 2.0% $\frac{W}{V}$ CCA, which showed less than 10% weight loss by the end of the burial period, only showed increases in nitrogen content up to the 6 week sampling interval.

Pine

Comparison of the nitrogen data for CCA treated pine centre blocks (Fig 2.3) and for ACA treated pine centre blocks (Fig 4.6) allows the following conclusions to be drawn:

1. Comparison of unburied control blocks shows that the ACA treated pine blocks contained considerably more nitrogen than the CCA treated blocks prior to soil burial: the nitrogen contents of ACA treated blocks ranged from 0.25 to 0.33% $\frac{W}{W}$ whereas the nitrogen content of CCA treated pine blocks was less than 0.1% $\frac{W}{W}$.

2. Comparison of the nitrogen contents of CCA and ACA treated lime blocks exhumed after 18 weeks of soil burial shows that, with the exception of the 0.142% $\frac{W}{V}$ ACA treated blocks, ACA treated pine blocks contained considerably more nitrogen than CCA treated blocks. Blocks treated with 0.012 and 0.028% $\frac{W}{V}$ ACA had nitrogen contents of nearly 0.4% $\frac{W}{W}$ after 18 weeks of soil burial

whereas blocks treated with 0.25 and 0.5% $\frac{W}{V}$ CCA reached a maximum nitrogen content of only 0.24% $\frac{W}{W}$ after 12 weeks.

Non-ammoniacal nitrogen data for ACA treated pine blocks (Fig 4.8) shows that inputs of nitrogen to wood blocks during soil burial only occurred where there was also significant decay. 0.012 and 0.028% $\frac{W}{V}$ ACA treated pine blocks showed continued increases in non-ammoniacal nitrogen content throughout the burial period and these increases amounted to about 0.2% $\frac{W}{W}$ nitrogen by the 18 week sampling interval. Pine blocks treated with 0.071 and 0.142% $\frac{W}{V}$ ACA showed no significant increases in non-ammoniacal nitrogen content.

CCA treated pine blocks (Fig 2.3) showed increases in nitrogen content at all preservative treatment levels, during the first 6 weeks of soil burial, regardless of whether or not the blocks subsequently decayed. These increases amounted to about 0.1% $\frac{W}{W}$ nitrogen. Only blocks treated with 0.25 and 0.5% $\frac{W}{V}$ CCA, which eventually showed signs of decay, showed continued increases in nitrogen content beyond 6 weeks, reaching 0.24% $\frac{W}{W}$ nitrogen at the 12 week sampling interval. The total nitrogen input to these blocks during soil burial was about 0.17% $\frac{W}{W}$ and was therefore less than that observed for 0.012 and 0.028% $\frac{W}{V}$ ACA treated blocks, although the latter were far more heavily decayed.

Fig. 4.1 Mean % weight loss for unleached and leached untreated, ammonia treated and ACA treated lime blocks during soil burial.

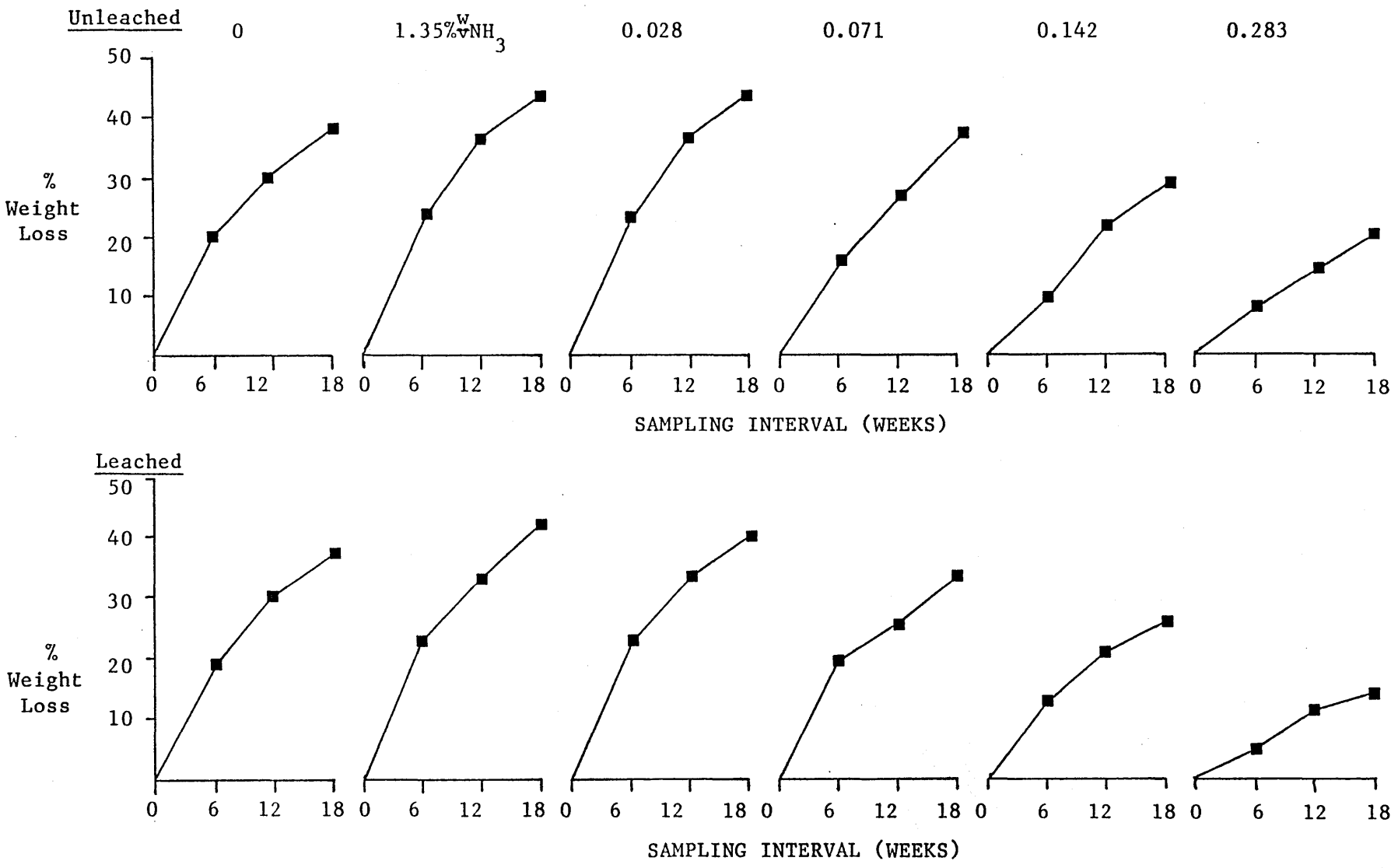

ACA TREATING CONCENTRATION (%w/v)
Unleached
0
1.35%w/vNH3
0.028
0.071
0.142
0.283
% Weight Loss
50
40
30
20
10
0 6 12 18
SAMPLING INTERVAL (WEEKS)
Leached
% Weight Loss
SAMPLING INTERVAL (WEEKS)

Fig. 4.2 Mean % weight loss for untreated, ammonia treated and ACA treated pine and spruce blocks during soil burial.

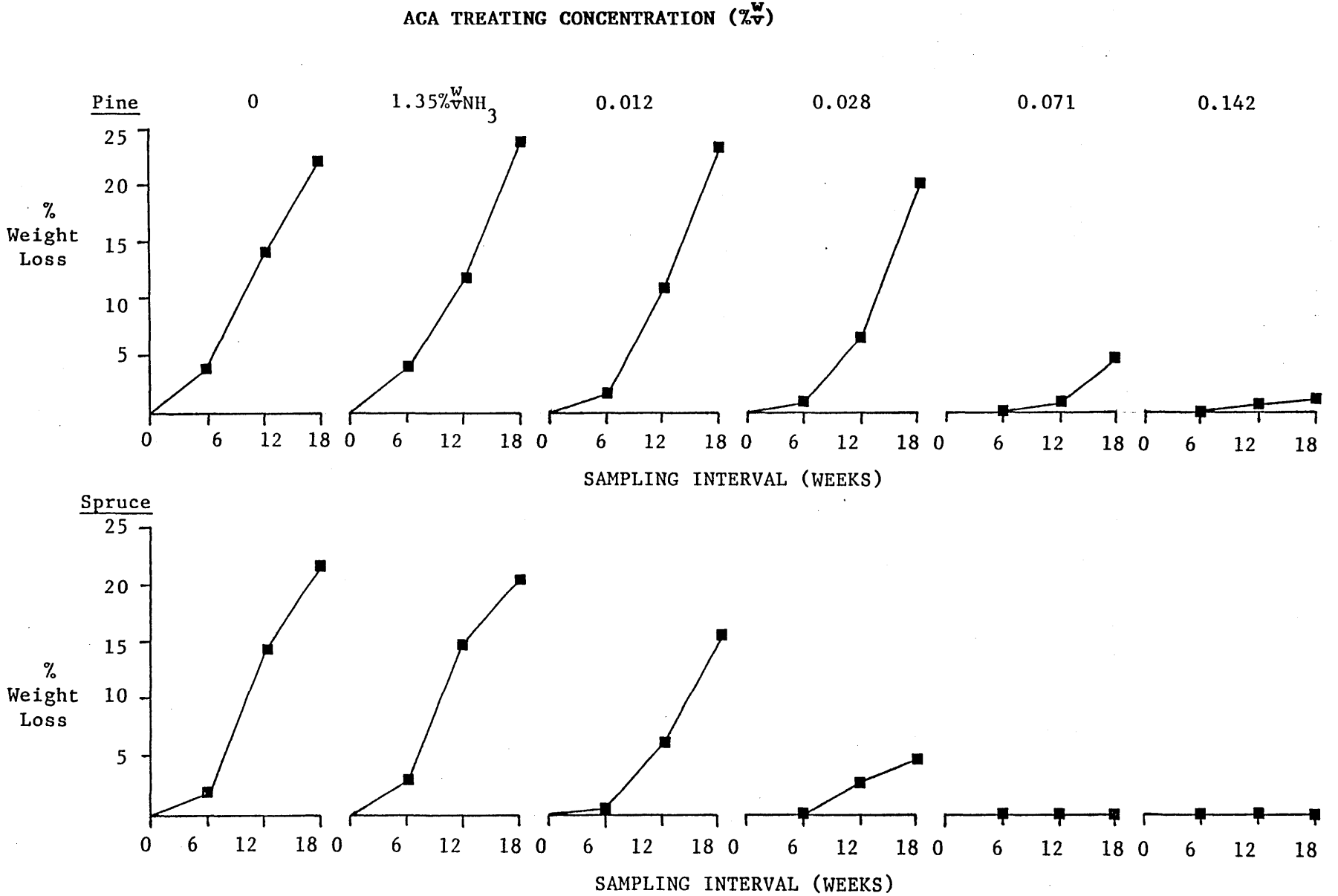

ACA TREATING CONCENTRATION (%w/v)
Pine
0
1.35%w/vNH3
0.012
0.028
0.071
0.142
% Weight Loss
25
20
15
10
5
0
6
12
18
SAMPLING INTERVAL (WEEKS)
Spruce
% Weight Loss
SAMPLING INTERVAL (WEEKS)

Fig. 4.3 Mean $\%\frac{w}{w}$ ammonium nitrogen contents of unleached and leached untreated, ammonia treated and ACA treated lime blocks during soil burial.

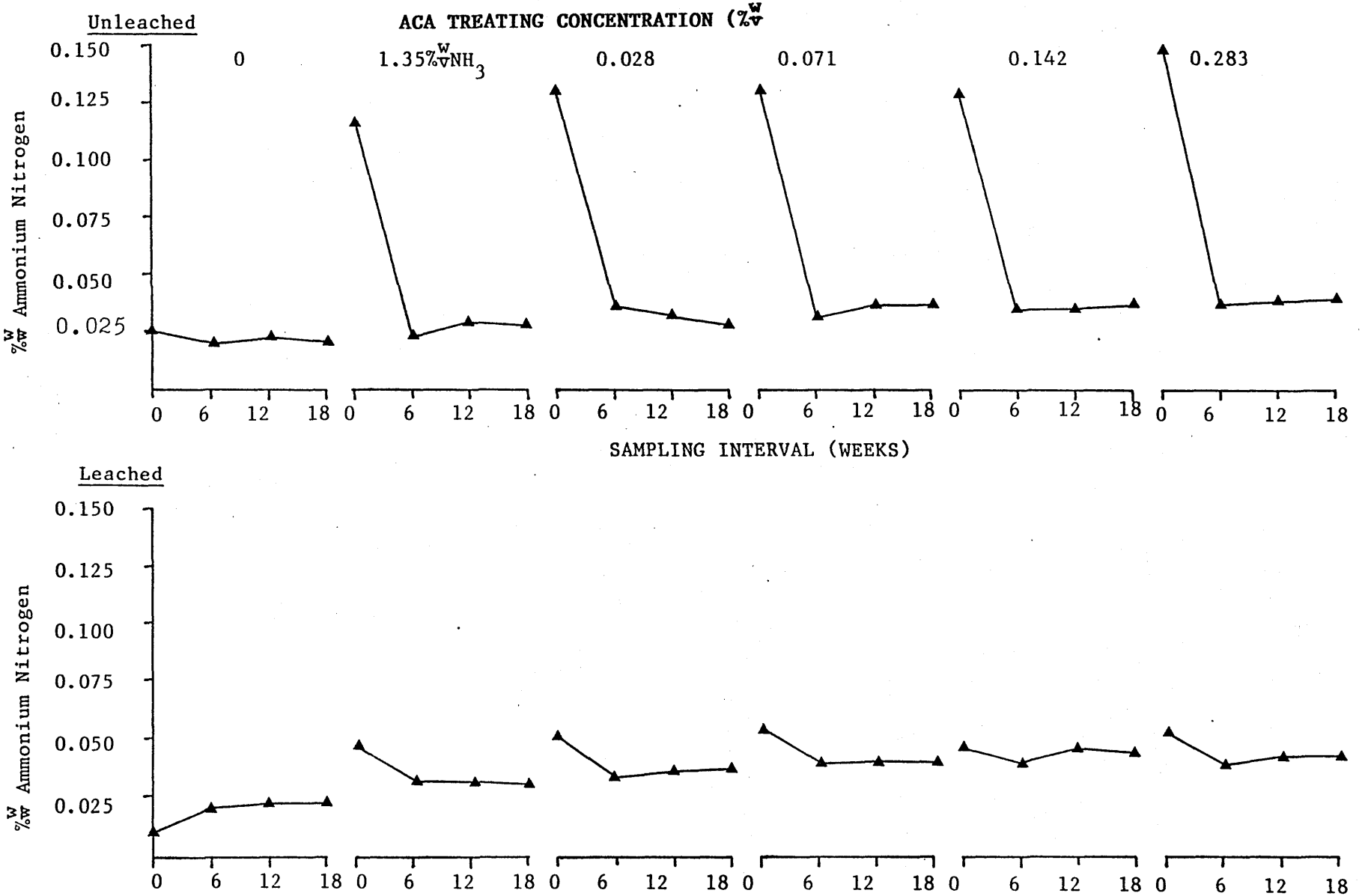

Unleached
ACA TREATING CONCENTRATION (%w/v)
0
1.35%w/vNH3
0.028
0.071
0.142
0.283
0.150
0.125
0.100
0.075
0.050
0.025
%w/w Ammonium Nitrogen
0 6 12 18
SAMPLING INTERVAL (WEEKS)
Leached

Fig. 4.4 Mean $\%\frac{w}{w}$ ammonium nitrogen contents of untreated, ammonia treated and ACA treated pine and spruce blocks during soil burial.

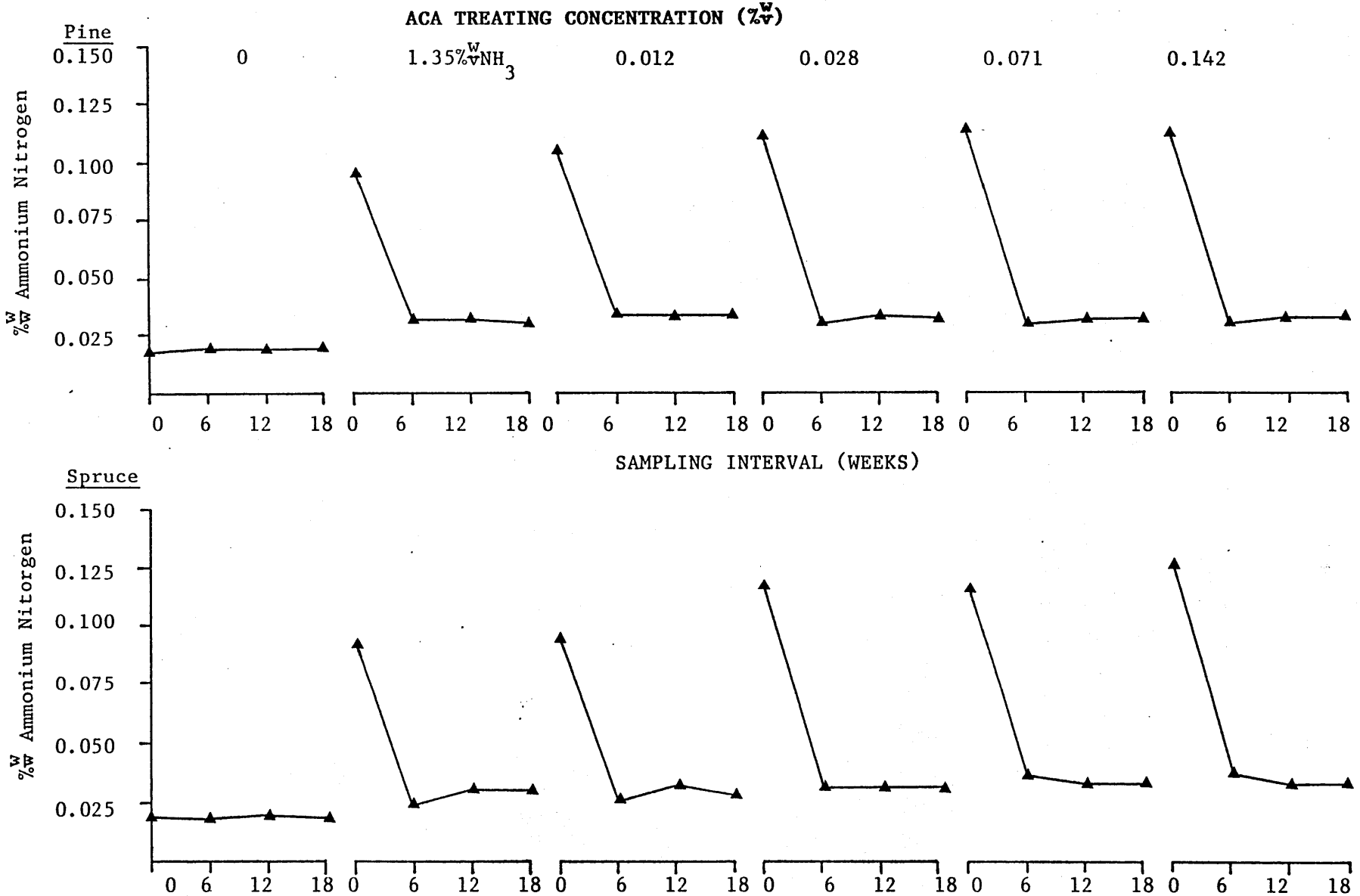

ACA TREATING CONCENTRATION (%w/v)
Pine
0
1.35%w/vNH3
0.012
0.028
0.071
0.142
%w/w Ammonium Nitrogen
0.150
0.125
0.100
0.075
0.050
0.025
0 6 12 18
SAMPLING INTERVAL (WEEKS)
Spruce
%w/w Ammonium Nitorgen

Fig. 4.5 Mean $\%\frac{w}{w}$ nitrogen contents of unleached and leached untreated, ammonia treated and ACA treated lime blocks during soil burial.

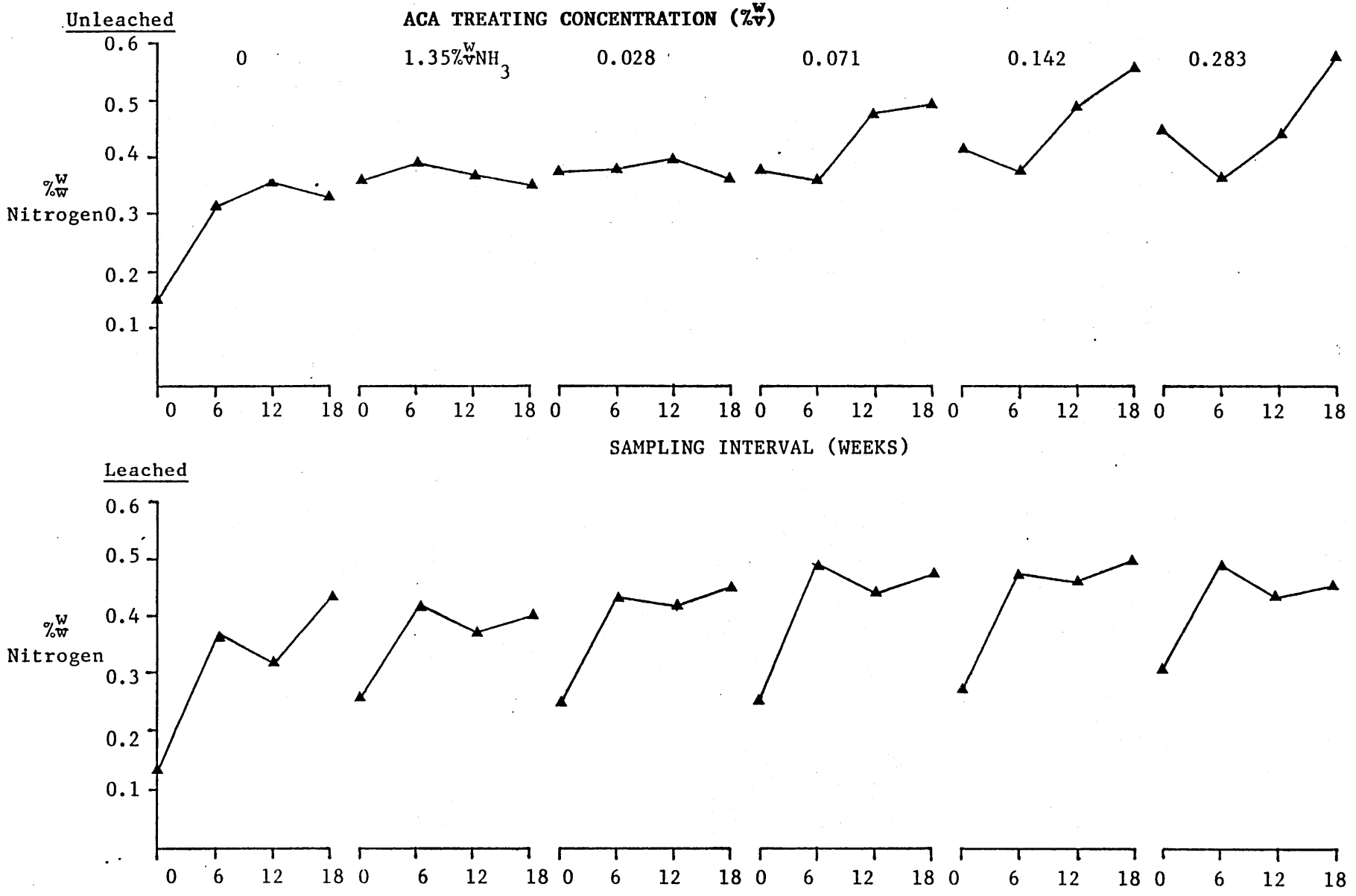

Unleached
ACA TREATING CONCENTRATION (%w/v)
0
1.35%w/vNH3
0.028
0.071
0.142
0.283
%w/w Nitrogen
0.6
0.5
0.4
0.3
0.2
0.1
0 6 12 18
SAMPLING INTERVAL (WEEKS)
Leached

Fig. 4.6 Mean $\%\frac{w}{w}$ nitrogen contents of untreated, ammonia treated and ACA treated spruce blocks during soil burial.

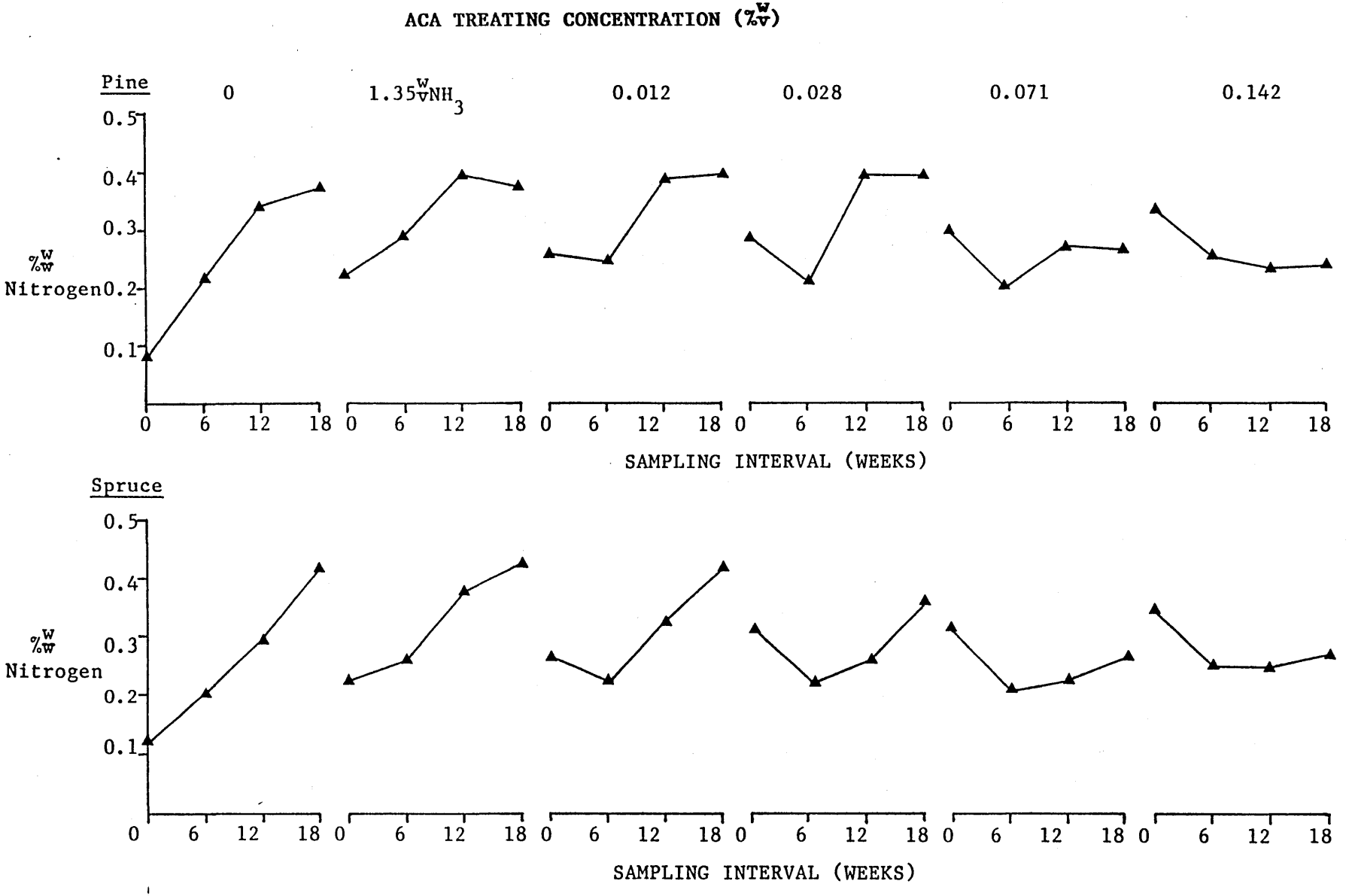

ACA TREATING CONCENTRATION (%w/v)
Pine
0
1.35%w/v NH3
0.012
0.028
0.071
0.142
%w/w Nitrogen
0.5
0.4
0.3
0.2
0.1
0 6 12 18
SAMPLING INTERVAL (WEEKS)
Spruce
%w/w Nitrogen
0.5
0.4
0.3
0.2
0.1
0 6 12 18
SAMPLING INTERVAL (WEEKS)

Fig. 4.7 Mean $\%\frac{w}{w}$ non-ammoniacal nitrogen contents of unleached and leached untreated, ammonia treated and ACA treated lime blocks during soil burial.

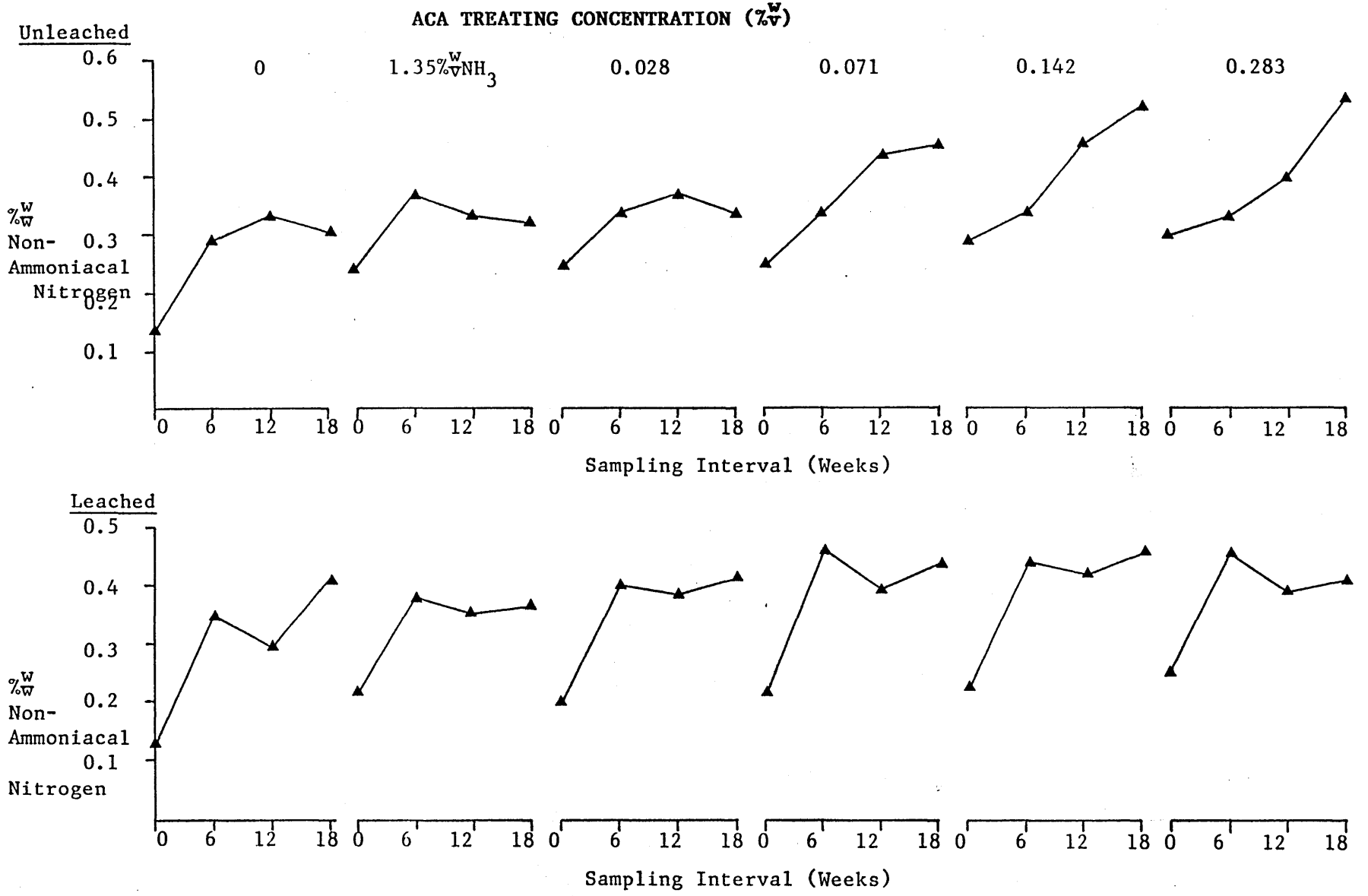

ACA TREATING CONCENTRATION (%w/v)
Unleached
0
1.35%w/vNH3
0.028
0.071
0.142
0.283
%w/w Non-Ammoniacal Nitrogen
0.6
0.5
0.4
0.3
0.2
0.1
0 6 12 18
Sampling Interval (Weeks)
Leached
0.5
0.4
0.3
0.2
0.1
%w/w Non-Ammoniacal Nitrogen
0 6 12 18
Sampling Interval (Weeks)

Fig. 4.8 Mean $\%\frac{w}{w}$ non-ammoniacal nitrogen contents of untreated, ammonia treated and ACA treated pine and spruce blocks during soil burial.

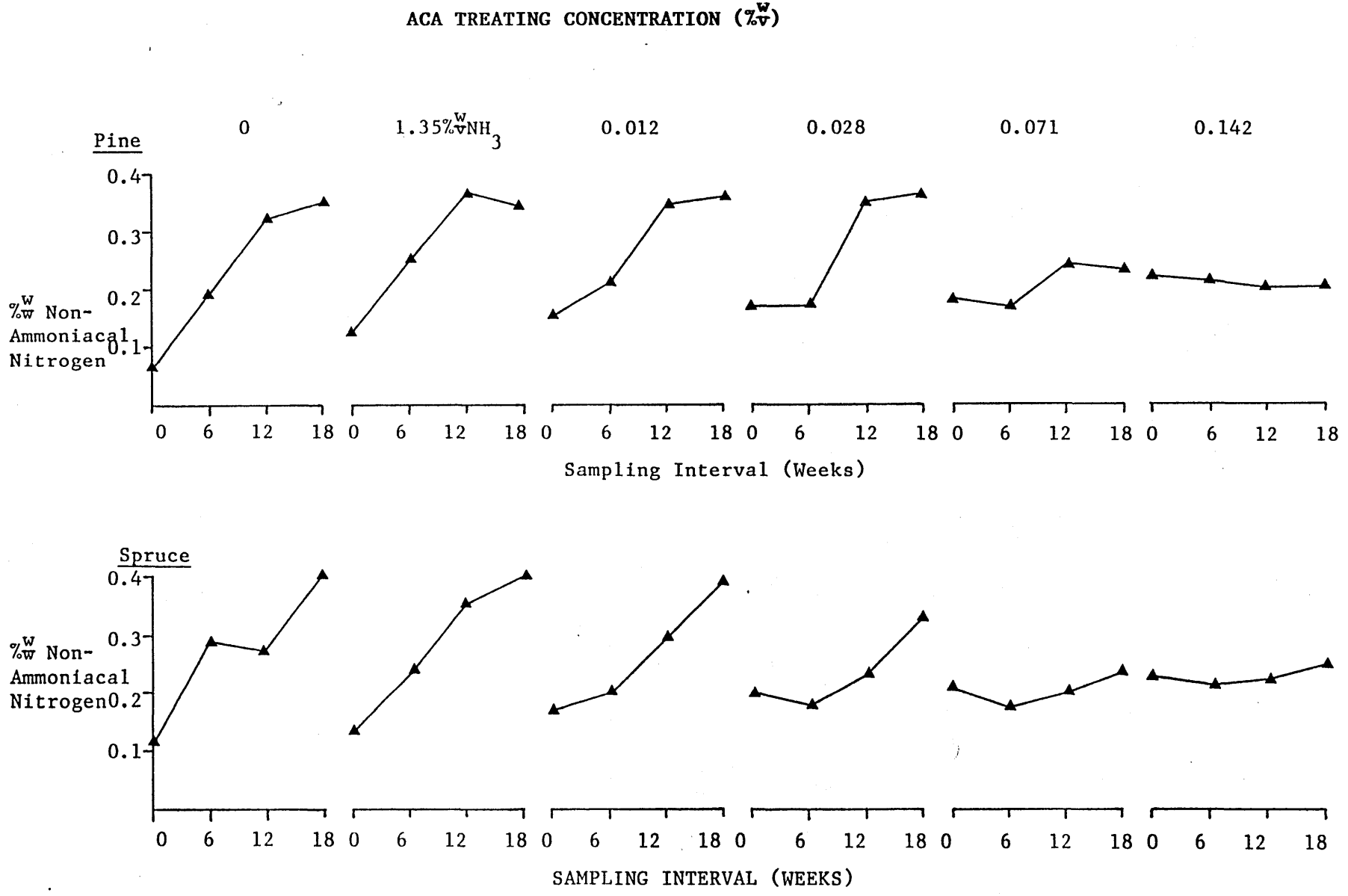

ACA TREATING CONCENTRATION (%w/v)
0
1.35%w/vNH3
0.012
0.028
0.071
0.142
Pine
%w/w Non-Ammoniacal Nitrogen
0.4
0.3
0.2
0.1
0 6 12 18
Sampling Interval (Weeks)
Spruce
%w/w Non-Ammoniacal Nitrogen
SAMPLING INTERVAL (WEEKS)

Fig. 4.9 Mean $\%\frac{w}{w}$ copper contents of unleached and leached untreated, ammonia treated and ACA treated lime blocks during soil burial.

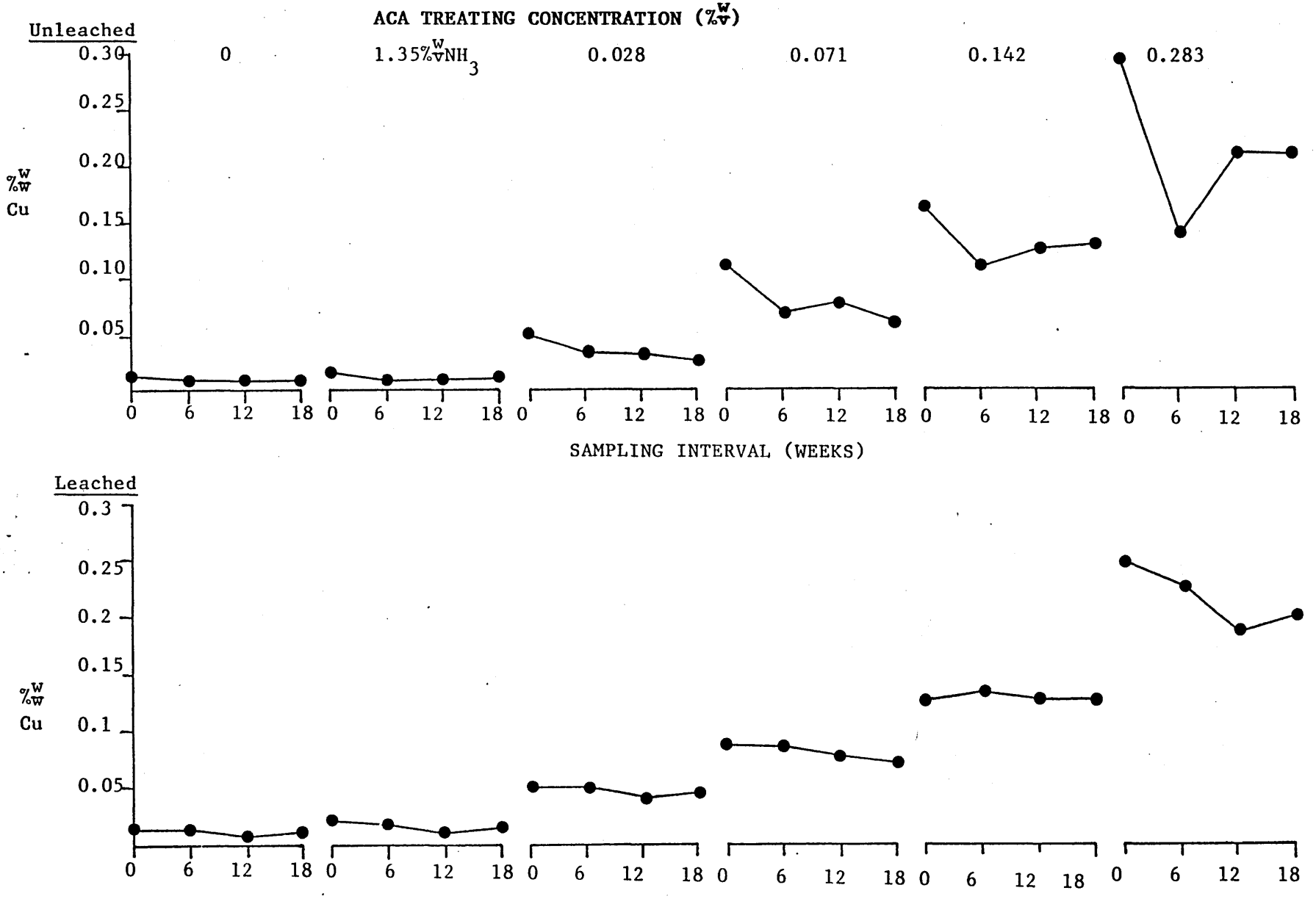

ACA TREATING CONCENTRATION (%w/v)
Unleached
0
1.35%w/vNH3
0.028
0.071
0.142
0.283
0.30
0.25
0.20
0.15
0.10
0.05
%w/w Cu
0 6 12 18
SAMPLING INTERVAL (WEEKS)
Leached
0.3
0.25
0.2
0.15
0.1
0.05
%w/w Cu
0 6 12 18

Fig. 4.10 Mean $\%\frac{w}{w}$ copper contents of untreated, ammonia treated and ACA treated pine and spruce blocks during soil burial.

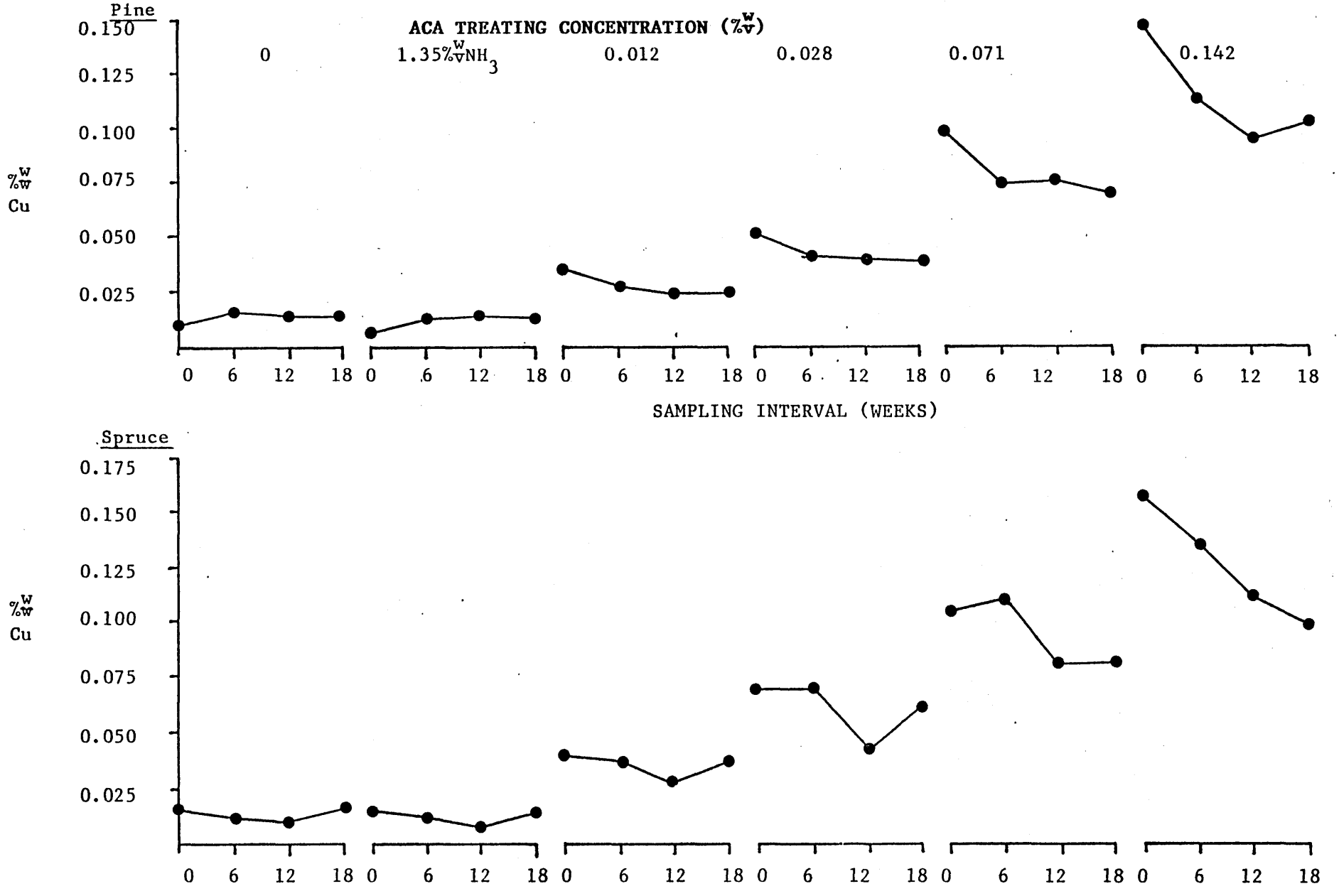

Pine
ACA TREATING CONCENTRATION (%w/v)
0
1.35%w/vNH3
0.012
0.028
0.071
0.142
0.150
0.125
0.100
0.075
0.050
0.025
%w/w Cu
0 6 12 18
SAMPLING INTERVAL (WEEKS)
Spruce
0.175
0.150
0.125
0.100
0.075
0.050
0.025
%w/w Cu
0 6 12 18

Table 4.4

Two-way analyses of variance to detect significance of differences in weight loss between leached and unleached lime blocks and between pine and spruce blocks during soil burial

Wood Types Compared	Treating Solution	Time Interval	Wood Type	Interaction
Unleached Lime Versus Leached Lime	Untreated	XXX	NS	NS
	1.35% $\frac{W}{V}$ NH_3	XXX	NS	NS
	0.028% $\frac{W}{V}$ ACA	XXX	NS	NS
	0.071% $\frac{W}{V}$ ACA	XXX	NS	X
	0.142% $\frac{W}{V}$ ACA	XXX	NS	NS
	0.283% $\frac{W}{V}$ ACA	XXX	XX	NS
Pine Versus Spruce	Untreated	XXX	NS	NS
	1.35% $\frac{W}{V}$ NH_3	XXX	NS	XX
	0.012% $\frac{W}{V}$ ACA	XXX	XXX	XXX
	0.028% $\frac{W}{V}$ ACA	XXX	XXX	XXX
	0.071% $\frac{W}{V}$ ACA	XXX	XX	XX
	0.142% $\frac{W}{V}$ ACA	NS	XXX	NS

XXX, XX, X and NS represent probabilities of <0.1, 1.0, 5 and > 5% respectively that differences arising from each column could arise by chance.

Table 4.5

Correlation coefficients of weight loss and non-ammoniacal nitrogen content for untreated, ammonia treated and ACA treated wood blocks during soil burial

Treating Solution	Wood Type			
	Unleached Lime	Leached Lime	Pine	Spruce
Untreated	0.859	0.866	0.927	0.951
1.35% $\frac{W}{V}$ NH_3	0.582	0.689	0.768	0.898
0.012% $\frac{W}{V}$ ACA	-	-	0.828	0.871
0.028% $\frac{W}{V}$ ACA	0.645	0.780	0.860	0.753
0.071% $\frac{W}{V}$ ACA	0.852	0.798	0.289	0.279
0.142% $\frac{W}{V}$ ACA	0.870	0.805	0.180	0.230
0.283% $\frac{W}{V}$ ACA	0.841	0.587	-	-

Table 4.6

Percentage loss of copper from ACA treated wood blocks during 18 weeks of burial in soil

Wood Type	ACA Treating Concentration (% $\frac{w}{v}$)	Percentage Loss of Copper
Unleached Lime	0.028	52.1
	0.071	47.2
	0.142	29.8
	0.283	29.4
Leached Lime	0.028	15.7
	0.071	20.5
	0.142	23.8
	0.283	18.8
Pine	0.012	31.4
	0.028	24.0
	0.071	28.6
	0.142	29.9
Spruce	0.012	5.3
	0.028	13.0
	0.071	22.9
	0.142	37.2

Table 4.7

One-way analyses of variance of copper contents of lime, pine and spruce blocks to detect significance of losses occurring during soil burial

Wood Type	ACA Treating Concentration (% $\frac{W}{V}$)				
	0.012	0.028	0.071	0.142	0.283
Unleached Lime	NT	***	***	***	***
Leached Lime	NT	NS	NS	NS	**
Pine	*	***	***	***	NT
Spruce	*	66	66	666	NT

***, **, * and NS represent probabilities of <0.1, 1.0, 5.0 and >5% respectively that changes in copper contents of blocks during soil burial could arise by chance.

NT = No trial

Table 4.8

Two-way analyses of variance to detect significance of differences in weight loss between CCA treated and ACA treated lime and pine centre blocks during soil burial

Wood Type	Preservative Treatments Compared	Interaction
Lime Centre	1.0% $\frac{W}{V}$ CCA versus 0.142% $\frac{W}{V}$ ACA	XXX
Pine Centre	0.25% $\frac{W}{V}$ CCA versus 0.012% $\frac{W}{V}$ ACA	XXX
Pine Centre	0.75% $\frac{W}{V}$ CCA versus 0.071% $\frac{W}{V}$ ACA	XXX

XXX represents a probability of <0.1% that differences in rates of decay of CCA and ACA treated wood blocks could arise by chance.

4.4 Discussion

In terms of the main aims of the ACA burial experiment, the following conclusions can be drawn:

1. The toxic thresholds of ACA in centre wood blocks of lime, pine and spruce were greater than 0.283% $\frac{w}{v}$, 0.142% $\frac{w}{v}$ and 0.071% $\frac{w}{v}$ respectively (Figs 4.1 and 4.2).

2. The toxic thresholds of the fungicide copper were higher in ACA treated wood than in CCA treated wood (Chapter 2): the toxic thresholds of copper in ACA treated lime and pine centre blocks were greater than 0.286% $\frac{w}{w}$ and 0.09% $\frac{w}{w}$ copper respectively whereas for CCA treated lime and pine centre blocks, the toxic thresholds were only 0.173% $\frac{w}{w}$ and 0.062% $\frac{w}{w}$ copper respectively.

The rate of decay of lime and pine centre blocks was also significantly faster when treated with ACA than when treated with CCA to similar pre-burial copper contents (Table 4.8).

3. ACA treated wood blocks contained considerably more nitrogen than untreated and CCA treated wood blocks prior to soil burial (Figs 2.2, 2.3, 4.5 and 4.6). After 18 weeks of soil burial, lime and pine blocks still generally contained more nitrogen when treated with ACA than when treated with CCA. These differences in nitrogen

content between ACA and CCA treated wood may partially account for the higher toxic thresholds of copper in ACA treated wood.

4. The ammonium nitrogen contents of unleached ammonia and ACA treated lime, pine and spruce blocks (Figs 4.3 and 4.4) fell considerably during the first 6 weeks of soil burial but after this sampling interval remained constant at a low level. The ammonium nitrogen contents of leached ammonia and ACA treated lime blocks, although lower than those of unleached blocks prior to soil burial, also fell during the first 6 weeks of burial to levels similar to those of unleached blocks and then similarly remained constant throughout the rest of the burial period.

5. Unleached ACA treated lime, pine and spruce blocks showed considerable losses of copper during soil burial (Figs 4.9 and 4.10). These losses of up to 50% (Table 4.6) were generally considerably greater than the 20% losses observed during aqueous leaching (Table 3.17). Leached ACA treated lime blocks also showed losses of copper during soil burial, although these losses only amounted to about 20%. Losses of copper from all ACA treated blocks generally occurred mostly during the first 6 weeks of soil burial, with subsequent losses being small.

In addition to the main conclusions outlined above, from the total nitrogen data (Figs 4.5 and 4.6) and the

non-ammoniacal nitrogen data (Figs 4.7 and 4.8) for ACA treated lime, pine and spruce blocks, further conclusions can be drawn:

1. The total nitrogen contents of ammonia and ACA treated lime, pine and spruce blocks (Figs 4.5 and 4.6) reflected losses of ammonium nitrogen during the first 6 weeks of soil burial. Therefore, increases in the total nitrogen content of these blocks during decay were not as large as increases observed in decaying CCA treated wood blocks (Chapter 2) and were underestimates of inputs of microbial nitrogen to wood.

2. Inputs of microbial nitrogen to ACA treated wood during soil burial, as measured by increases in the non-ammoniacal nitrogen contents of blocks, were considerable in all blocks which showed decay.

With the exception of unleached 0.028% $\frac{W}{V}$ ACA treated lime blocks and those ACA treated pine and spruce blocks which did not decay, all unleached ACA treated lime, pine and spruce blocks showed continued increases in non-ammoniacal nitrogen content during decay throughout the burial period. Leached ACA treated lime blocks and unleached lime blocks treated with 0.028% $\frac{W}{V}$ ACA showed large increases in non-ammoniacal nitrogen content during the first 6 weeks of soil burial, but showed no further increases beyond this time, despite continued decay up to the 18 week sampling interval.

3. ACA treated lime and pine blocks generally showed larger inputs of microbial nitrogen during decay than similar wood blocks treated with CCA, although these higher nitrogen inputs may be accounted for by the much higher weight losses observed in the ACA treated blocks.

Untreated blocks of all wood types showed continuous decay throughout the 18 week burial period (Figs 4.1 and 4.2). The decay curves for these blocks were similar to those found for untreated control blocks in the CCA burial experiment (Chapter 2), although the lime blocks decayed more slowly in the present experiment.

The treatment of lime, pine and spruce blocks with ammonia in the absence of copper and arsenic did not significantly affect the rate of decay relative to untreated blocks (Figs 4.1 and 4.2). This observation is similar to the observation of Chapter 2 that surface nutrients did not significantly affect the rate of decay of untreated lime and pine blocks during an 18 week soil burial period. In the CCA burial experiment, the effect of surface nutrients on the decay rate was only obvious in preservative treated wood, where the nutrients considerably reduced the toxicity of the preservative elements. It appears that the ammonia present in ACA treated wood may have acted in a similar way in the present study by reducing the toxicity of the fungicide copper.

The rates of decay of blocks of all wood types when treated with higher concentrations of ACA were slower than those of untreated blocks (Figs 4.1 and 4.2) and blocks of both pine and spruce were protected at the 18 week sampling interval by 0.142% $\frac{W}{V}$ ACA. Therefore, the presence of copper and arsenic in the wood clearly interfered with the decay process, either by direct toxicity to micro-organisms or by acting as a physical barrier to decay. However, lime and pine blocks treated with the lowest concentrations of ACA apparently decayed faster than untreated blocks. Therefore, in these blocks, the high nitrogen content more than compensated for the toxic effects of the preservative elements.

Untreated pine and spruce blocks decayed considerably more slowly than untreated lime blocks (Figs 4.1 and 4.2): weight loss values after 18 weeks of soil burial were about 38% and about 24% for lime blocks and softwood blocks respectively. Ammonia treated and ACA treated pine and spruce blocks also decayed at a slower rate than lime blocks treated with the same preservative concentration. These differences in decay rates between softwoods and the hardwood lime, both in the untreated and preservative treated form are similar to the findings for untreated and CCA treated lime and pine blocks in the CCA burial experiment (Chapter 2) and reflect the higher natural decay resistance of softwoods than hardwoods.

Statistical comparison of the weight loss values of leached and unleached untreated lime blocks (Table 4.4) showed that aqueous leaching had no significant effect on the subsequent decay rate during soil burial. Graphs of weight loss data for leached and unleached ammonia and ACA treated lime blocks (Fig 4.1) suggest that, at each treatment level, the rate of decay was lower in leached blocks than in the unleached blocks. However, statistical analysis of the same weight loss data (Table 4.4) showed that there were generally no significant differences between the weight loss values of the leached and unleached blocks at each ammonia or ACA treating concentration, despite the fact that the nitrogen contents of unleached blocks were more than 0.1% $\frac{w}{w}$ higher than those of leached blocks at all treatment levels. This suggests that the soluble nitrogen component, present only in the unleached blocks at the time of burial, does not accelerate decay, possibly due to its rapid loss to the soil as a result of leaching. Therefore, any stimulation of the decay rate in ACA treated wood as a result of the extra nitrogen present may be caused by the insoluble nitrogen remaining in the wood after aqueous leaching.

The toxic thresholds of copper in both lime and pine centre blocks were higher in ACA treated wood (Figs 4.1 and 4.2) than in CCA treated wood (Chapter 2, Figs 2.2 and 2.3). In the CCA burial experiment, lime and pine centre

were protected (less than 3% weight loss after 18 weeks of soil burial) by 2% $\frac{w}{v}$ CCA (0.21% $\frac{w}{w}$ copper) and 0.5% $\frac{w}{v}$ CCA (0.062% $\frac{w}{w}$ copper) respectively. In this experiment, lime was not protected by 0.283% $\frac{w}{v}$ ACA (0.286% $\frac{w}{w}$ copper) and pine was protected by 0.142% $\frac{w}{v}$ ACA (0.147% $\frac{w}{w}$ copper). These findings are in sharp contrast with those of Hulme and Butcher (1977c) who found, during pure culture studies, that CCA and ACA treated hardwoods had similar toxic thresholds of copper.

Statistical analysis of the weight loss data from CCA and ACA treated lime and pine blocks with similar copper loadings (Table 4.8) showed that the rate of decay of blocks of both wood types was significantly faster when treated with ACA than when treated with CCA to similar pre-burial copper contents. This faster decay rate was observed in ACA treated lime blocks despite the fact that untreated lime control blocks decayed significantly more slowly than in the CCA burial experiment (weight loss values after 18 weeks were 57.9 and 38% for the CCA and ACA burial experiments respectively). Smith (1980) considered that such differences in decay rates between different studies using identical experimental conditions were caused by differences in the virulence of the soil microflora. Untreated pine blocks decayed at a similar rate in both the CCA and ACA burial experiments, reaching about 20% weight loss after 18 weeks of soil burial.

The higher toxic thresholds of copper and the higher rates of decay observed in ACA treated wood compared to CCA treated wood may be due to a stimulation of decay by the extra nitrogen in ACA treated wood. Such nitrogen, probably in the form of ammonium ions, might act as a stimulant to decay either by acting as a source of nitrogen to micro-organisms entering the wood or by causing a chemostimulation of the soil microflora and thus stimulating a microbial invasion of the wood. Also, the elevated nitrogen levels in ACA treated wood might directly influence the toxicity of copper, as shown for CCA treated wood with added nitrogen by Henningsson (1976).

An alternative reason for the high toxic thresholds of copper in ACA treated wood is that the copper may be in a form less toxic to wood decaying micro-organisms than the copper in CCA treated wood. Since much of the copper in ACA treated wood is thought to be in the form of precipitates not chemically bound to the lignin or cellulose of the wood substance (Hulme, 1979), such precipitated copper would not become concentrated in the cell walls of wood fibres and tracheids during fixation and would therefore not be active against micro-organisms decaying the wood cell walls. Copper precipitated in the cell walls but not chemically bound to the wood might not be solubilised during the decay process and therefore might also be inactive against wood decaying micro-organisms.

Copper fixed to the cell walls of fibres and tracheids of ACA treated wood by cation exchange mechanisms is likely to be most active in the protection of the wood against decay.

Copper is generally considered to be the main toxic element to fungi in CCA (Hulme and Butcher, 1977a). However, if chromium and arsenic do have fungicidal properties, ACA treated wood may be considerably less toxic than CCA treated wood containing a similar amount of copper; ACA treated wood contains no chromium and also contains considerably less arsenic at any given copper concentration than CCA treated wood due to the higher atom ratio of copper to arsenic in ACA than in CCA (1.61 : 1 and 1 : 1.06 for ACA and CCA respectively as used in these studies).

The toxic thresholds of ACA were lower in spruce than in pine, being 0.071 and 0.142% $\frac{W}{V}$ ACA for spruce and pine respectively (Fig 4.2) and statistical analysis of the weight loss data (Table 4.4) shows that the levels and rates of decay in spruce blocks were significantly lower than in pine blocks at all treating concentrations where decay occurred. There were no significant differences between the rates of decay of untreated pine and spruce blocks and therefore the better performance of ACA treated spruce can not be attributed to better natural decay resistance. Copper and nitrogen contents for ACA treated blocks of the two wood types were also very similar.

It therefore appears that ACA was in a more toxic or available form in spruce blocks than in pine blocks. Problems of preservative penetration of spruce due to its refractory nature were minimised by the small size of the blocks used. Therefore, the good performance of ACA treated spruce in this experiment cannot be considered an indication of the performance of large pieces of timber in the field where problems of macrodistribution of preservative may occur.

The ammonium nitrogen data (Figs 4.3 and 4.4) clearly show that the ammonium nitrogen contents of ammonia and ACA treated blocks of all wood types fell during the first 6 weeks of soil burial. This loss of ammonia from the wood may be as a result of leaching or due to uptake and conversion of ammonia to other nitrogenous compounds by micro-organisms in the wood (or a combination of both). Ammonia and ACA treated lime blocks which had been leached prior to soil burial still showed a small fall in ammonium nitrogen content, suggesting that the soil solution or micro-organisms solubilised some ammonium nitrogen resistant to aqueous leaching. Ammonium ions fixed to cation exchange sites on wood might be subject to such solubilisation.

After the first 6 weeks of soil burial, the ammonium nitrogen contents of all ammonia and ACA treated wood blocks remained stable at levels slightly above those of

untreated blocks. This residual ammonium nitrogen probably represents ammonia complexed to acidic or phenolic groups of lignin and cellulose in wood. Exhumed ACA treated wood blocks contained slightly more ammonium nitrogen than exhumed ammonia treated blocks, suggesting that even after exposure to soil, some ammonia was still associated with preservative elements.

Total nitrogen data for untreated lime, pine and spruce blocks (Figs 4.5 and 4.6) show that the nitrogen contents of all wood types except unleached lime increased continuously throughout the 18 week burial period. Decay was also continuous throughout this period and there was a good correlation between weight loss and nitrogen content for all wood types (Table 4.5). This pattern of nitrogen increase during decay corresponds to that observed during previous soil burial studies on untreated wood (King, Oxley and Long, 1976; Waite and King, 1979) and for untreated wood blocks in the CCA burial experiment (Chapter 2). King, Mowe, Smith and Bruce (1981) considered that nitrogen increases they observed in buried blocks during decay were due largely to a continuous input of microbial biomass from soil to wood as a result of chemo-stimulation of soil microflora by the wood, with a constant mycelial connection between the wood and soil.

The rate of increase in nitrogen content of untreated blocks was similar for all wood types. This finding

contrasts with that of the CCA burial experiment (Chapter 2) where higher rates of increase in nitrogen content were observed in lime and beech blocks than in pine blocks. These differences in rates of nitrogen increase were attributed to the hardwood blocks evoking a greater chemostimulatory response in the soil microflora than the softwood blocks. The untreated lime blocks showed much smaller increases in nitrogen content during this experiment (Fig 4.5) than untreated lime centre blocks in the CCA burial experiment (Fig 2.2) whereas untreated pine blocks showed larger nitrogen increases in this experiment (Figs 4.6 and 2.3). These differences in the size of nitrogen increase in untreated blocks between experiments, possibly as a result of differences in the virulence of the soil microflora, may account for the failure to observe different rates of nitrogen increase between hardwood and softwood blocks in this experiment.

Total nitrogen data for unleached ammonia and ACA treated wood blocks of all wood types (Figs 4.5 and 4.6) reflect the fall in ammonium nitrogen concentration of the wood during the first six weeks of burial in soil. At lower ACA treating concentrations, the total nitrogen content remained constant or rose slightly during the first six weeks of soil burial, but at higher treating concentrations, the total nitrogen concentration fell over this period. At low treating concentrations, either some of the leachable ammonia was taken up by micro-organisms in the wood and therefore retained (as

non-ammoniacal nitrogen) or the loss of ammonia was counteracted by an input of microbial nitrogen as a result of microbial invasion of the wood. At higher ACA treating concentrations, the preservative concentration may have reduced microbial activity in the wood, thus allowing larger leaching losses of ammonia and reducing the microbial input of nitrogen.

Increases in the total nitrogen concentration of unleached ammonia and ACA treated blocks of all wood types did generally occur during the six to eighteen week period of burial, wherever decay occurred. These nitrogen increases are similar to those observed in decaying CCA treated wood (King, Smith, Baecker and Bruce, 1981 and Chapter 2 of this thesis). They cannot be attributed to inputs of soil salts to wood blocks, since pine and spruce blocks showing no decay also showed no increases in nitrogen content. Pine and spruce blocks treated with 0.071 and 0.142% $\frac{W}{V}$ ACA did not show significant nitrogen increases and showed little or no weight loss during the eighteen week burial period. King, Smith, Baecker and Bruce (1981) also found no nitrogen increases in buried lime blocks, containing very high concentrations of CCA, which had not decayed. However, this is in contrast with the CCA burial programme (Chapter 2) where considerable nitrogen increases during burial were observed even in those blocks which did not decay.

The lack of nitrogen inputs to undecayed pine and spruce blocks in this experiment may be due to soluble copper and arsenic leaching from the blocks reducing microbial activity in the surrounding soil. If the chemostimulatory response of micro-organisms to untreated wood (as shown by the rate of nitrogen inputs to wood) is lower for softwoods such as pine than for the hardwood lime, as suggested by the results of Chapter 2, the microbial activity should be lower in the soil around softwood blocks than around hardwood blocks. Therefore lower concentrations of copper and arsenic should be required to prevent microbial activity in the soil around softwood blocks and thus prevent microbial invasion of the wood.

Non-ammoniacal nitrogen data (Figs 4.7 and 4.8) show that the concentration of nitrogen in forms other than ammonium nitrogen increased during the first 6 weeks of soil burial in all ammonia and ACA treated lime blocks and in all pine and spruce blocks which showed immediate decay. These increases in non-ammoniacal nitrogen content give estimates of inputs of microbial nitrogen to blocks during soil burial. Therefore, up to the 6 week sampling interval, all ammonia and ACA treated blocks which showed decay also experienced inputs of nitrogen of a microbial source.

In unleached ammonia and ACA treated lime blocks and ammonia treated pine and spruce blocks, increases in non-ammoniacal nitrogen content and hence inputs of microbial

nitrogen generally continued throughout the burial period in a manner similar to that observed for decaying CCA treated wood. Pine and spruce blocks treated with 0.028% $\frac{w}{v}$ ACA only showed increases in non-ammoniacal nitrogen content beyond the 6 week sampling interval, corresponding with the onset of decay. In unleached ACA treated lime, pine and spruce blocks, there was a fairly close correlation between weight loss and non-ammoniacal nitrogen content (Table 4.5), indicating a close relationship between microbial inputs of nitrogen to wood and decay. This is in contrast with weight loss and nitrogen data for CCA treated wood (Figs 2.2 - 2.4), since for CCA treated wood, increases in nitrogen content generally preceded decay and correlation between weight loss and nitrogen content was therefore less marked (Table 2.5).

In the case of CCA treated wood in Chapter 2, it was considered that increases in the nitrogen content of the wood were required prior to decay in order to produce threshold nitrogen or microbial levels above which decay could occur. In ACA treated wood, however, the pre-burial nitrogen content was considerably higher than that of CCA treated wood and may already have been sufficient to support soft-rot decay. Therefore, decay of wood treated with ACA to sub-toxic levels might begin as soon as micro-organisms enter the wood.

The total nitrogen and non-ammoniacal nitrogen data for leached ammonia and ACA treated lime blocks (Figs 4.5 and 4.7) were very different from those for unleached lime blocks. There was a considerable increase in both the total nitrogen and non-ammoniacal nitrogen contents of all leached lime blocks during the first 6 weeks of soil burial. This is probably because the fall in ammonium nitrogen content of these blocks over the first 6 weeks of soil burial was comparatively small (only about 0.02% $\frac{w}{w}$ nitrogen compared to up to over 0.1% $\frac{w}{w}$ nitrogen in all unleached lime blocks). Between 6 and 18 weeks of soil burial, leached ammonia and ACA treated lime blocks showed no further increase in either total or non-ammoniacal nitrogen contents despite continued weight loss at a rate similar to that of unleached lime blocks at all treating concentrations. This suggests that, beyond the six week sampling interval, micro-organisms were not entering the leached blocks from the soil. It is unlikely that the blocks were saturated with micro-organisms from the soil, since in the CCA burial experiment (Chapter 2), nitrogen increases (considered to be indicative of movement of micro-organisms into wood) of up to 0.4% $\frac{w}{w}$ were observed in lime blocks, whilst nitrogen increases observed in leached blocks in this experiment only amounted to 0.25% $\frac{w}{w}$ at the most. However, it is possible that the micro-organisms responsible for the decay of leached lime blocks between six and eighteen weeks of burial in soil

were growing at the expense of nitrogen already present within the wood. Basidiomycete fungi might be responsible for this decay, since decay of wood by these fungi is not always associated with increased nitrogen concentrations in the wood (Klingstrom and Oksbjerg 1963; King and Waite, 1979). These fungi have the ability to decay wood using only the low concentrations of nitrogen present naturally in wood, possibly by re-utilising mycelial nitrogen released on autolysis (Cowling and Merrill, 1966) and therefore require no contact of the wood with soil or input of nitrogen from soil for decay to occur. Soft-rot fungi are considered to require a threshold of at least 0.2% $\frac{w}{w}$ nitrogen in wood before measurable decay can occur (Merrill and Cowling, 1966) and therefore require an input of nitrogen to the wood from soil before decay can occur. However, in ACA treated wood, the nitrogen concentration is well above this 0.2% threshold prior to soil burial and may be high enough to support decay activity by soft rot microfungi without any requirement for translocation of nitrogen from the soil.

It is not clear why the nitrogen dynamics of decay of leached ammonia and ACA treated blocks should be so different from those of unleached blocks, since leached and unleached lime blocks were buried together in the same soil boxes. However, the lack of soluble nitrogen in leached blocks on emplacement in soil must have reduced the

chemostimulation of the soil microflora, when compared to unleached blocks and leached ACA treated lime blocks also released smaller amounts of copper and arsenic into the surrounding soil. These differences in conditions between the soil around leached and unleached blocks may have led to differences between the primary microbial colonisers of the two types of block and consequently to the different nitrogen dynamics of decay observed.

Statistical analysis of the copper data for ACA treated wood blocks (Table 4.7) shows that significant losses of copper occurred from all unleached ACA treated blocks during soil burial. Unleached ACA treated lime blocks showed decreasing percentage losses of copper with increasing preservative treating concentration (Table 4.6). In contrast, ACA treated spruce blocks showed increasing percentage losses with increasing treating concentration. Pine blocks, however, showed similar percentage losses of copper at all ACA treating concentrations. In aqueous leaching studies (Chapter 3), ACA treated blocks of all three wood types showed similar percentage losses (about 20%) of copper at all preservative treating concentrations. There is therefore no clear reason for the discrepancies in percentage loss of copper with ACA treating concentration between blocks of the three wood types during soil burial.

With the exception of 0.012 and 0.028% $\frac{w}{v}$ ACA treated spruce blocks, all unleached ACA treated wood blocks showed larger percentage losses of copper during soil burial (Table 4.6) than during aqueous leaching (Chapter 3, Table 3). This suggests that either chemical components of soil such as organic acids or the soil microflora solubilised some extra copper not soluble in the distilled water used in the aqueous leaching studies. Since the main mechanism of fixation of ACA to wood is thought to involve the formation of precipitates such as copper arsenates and copper hydroxides (see Chapter 3), copper in ACA treated wood might be far more readily solubilised by acidic soil compounds or by acidic fungal secretions (Levi, 1976) than the copper in CCA treated wood.

The percentage losses of copper from the unleached ACA treated blocks were considerably larger than those observed from CCA treated blocks (Chapter 2), particularly at higher preservative treatment levels. This depletion of copper in the ACA treated blocks during soil burial may have considerably reduced the toxicity of the wood and may therefore represent another factor responsible for the poor performance of the preservative in this experiment.

Although leached ACA treated lime blocks did apparently show losses of copper of up to 20% during soil burial (Table 4.6); these losses were not statistically significant (Table 4.7). This suggests that although

unleached ACA treated blocks showed large losses of copper, the effect of chemical and biological components of the soil on the stability of copper in ACA treated wood was minimal.

The fall in the copper contents of all ACA treated blocks generally occurred mostly during the first 6 weeks of soil burial (Figs 4.9 and 4.10). Any further copper losses beyond this sampling interval were small and there was therefore an effective increase in the concentration of copper (on a % $\frac{w}{w}$ basis) in the residual wood as decay continued. This finding is identical to that of the CCA burial experiment (Chapter 2) where copper, chromium and arsenic became concentrated in wood during decay and suggests that the copper in ACA treated wood is not complexed to a part of the wood susceptible to soft-rot decay. The copper may instead be complexed with lignin or may be deposited in the form of a precipitate not complexed to wood and not rendered soluble by the decay process. Alternatively, copper released from wood during decay may have become complexed with dead microbial remains in the wood.

From the results of this burial experiment, it can be concluded that, for both the hardwood lime and the softwood pine, ACA was far less effective at protecting wood blocks from decay in soil than was CCA at similar copper loadings. The higher toxic thresholds of copper observed in ACA treated

wood may be due, in part, to the presence of a high concentration of nitrogen in the wood, both before and during burial in soil, which may have caused a stimulation of the decay process; the soluble, leachable fraction of this residual extra nitrogen might cause a chemostimulatory response of the soil microflora, leading to increased microbial invasion of the wood and insoluble nitrogen, remaining in ACA treated wood after the loss of the leachable fraction to the soil, might act as a source of nutrients to micro-organisms decaying the wood. However, the lack of chromium in ACA and its low arsenic content as compared to CCA may also have influenced the toxic thresholds of copper in ACA treated wood. In addition, the large percentage losses of copper observed from ACA treated wood may have further reduced the toxicity of the wood. From the information available, it is impossible to quantify the importance of each of these factors in determining the performance of ACA treated wood.

The high nitrogen content of ACA treated wood clearly does play an important part in its rapid decay in soil since, in contrast with CCA treated wood, ACA treated wood required no inputs of nitrogen from the soil before decay commenced. This suggests that the ACA treated wood already contained sufficient nitrogen to support microbial decay at the time of soil burial, allowing the first fungal colonisers of the wood to cause decay immediately. Therefore, whilst microbial invasion of ACA treated wood in soil (as

shown by increases in non-ammoniacal nitrogen content) clearly occurred, and in most cases continued throughout the decay process, it may not be an essential part of the mechanism of decay of the wood. This view is supported by the fact that leached lime blocks showed no increases in non-ammoniacal nitrogen content beyond the 6 week sampling interval, despite continued decay.

The results of this burial experiment also bring into question the use of pure culture studies such as those of Hulme and Butcher (1977c) in determining the performance of preservatives in wood in soil contact. Leaching losses of toxic elements and soluble nitrogenous compounds from ACA treated wood cannot be as severe on solid agar media as in soil systems. Therefore, chemostimulatory effects of the wood on micro-organisms and de-toxification of the wood as a result of leaching losses of toxic elements would be far greater in a soil burial experiment and may explain the better performance of ACA treated wood in the studies of Hulme and Butcher than in the present experiment. Pure culture studies also take no account of the possible importance of mixed microbial populations, including bacteria and actinomycetes as well as diverse types of wood decaying fungi, on the decay of preservative treated wood.

The concentrations of ACA used in this burial experiment were selected to produce concentrations of copper, in wood

blocks, similar to those in the CCA burial experiment. However, these ACA concentrations are well below normal commercial concentrations (which may be as high as 3% $\frac{w}{v}$) and therefore do not take full advantage of the high copper content of the preservative.

The ACA treating concentration selected may influence the performance of the treated timber in other ways. Although the nitrogen content of ACA treated wood increases with increasing preservative treating concentration, nitrogen content is not proportional to copper concentration (Chapter 3) and the ratio of copper to nitrogen rises with increasing ACA treating concentration. Therefore the effect of the nitrogen in ACA treated wood on preservative toxicity may not be as great at high preservative loadings as it was at preservative loadings used in this burial experiment. Also, if some copper in ACA treated wood is fixed by cation exchange mechanisms, as proposed by Hulme (1979), cation exchange sites should rapidly become saturated with copper during impregnation. Therefore, with increasing preservative treating concentration, a reducing proportion of the total copper in ACA treated wood should be fixed to cation exchange sites, leaving more available for the formation of copper hydroxide and copper arsenate precipitates. This should in turn lead to a higher proportion of the arsenic, readily leachable at lower ACA treating concentrations (Rak, 1976; Wilson Tamblyn and McCarthy, 1959), being retained in the wood in an insoluble form.

Therefore, the results of this experiment may not be representative of the performance of ACA in service timber. Further, longer term soil burial studies using hardwood and softwood blocks treated with higher concentrations of ACA would be required in order to establish a true laboratory representation of the processes occurring at the surface of ACA treated timber in service in soil contact. However, ACA treated wood, in addition to its high nitrogen content also appears to suffer all of the problems suffered by CCA treated wood when emplaced in soil: ACA treated wood is subject to microbial invasion as a result of chemostimulation of the microflora in the surrounding soil and is also subject to considerable depletion of copper as a result of leaching. This depletion of copper may be compounded by further solubilisation or immobilisation of copper by micro-organisms in the wood.

The high copper loadings present in commercial ACA treated timber may prove toxic to soil microflora and therefore confer protection on the timber. However, in order to prevent microbial invasion of the wood, some of the preservative must be in a soluble form capable of sterilising the surrounding soil, as described for CCA treated wood by Smith (1980). Thus there should be a gradual depletion of preservative from within the wood until the preservative concentration is no longer high enough to prevent microbial invasion and consequent decay. Therefore the eventual failure of all ACA treated wood seems inevitable.

CHAPTER 5

THE ROLE OF LIGNIN IN THE FIXATION OF NITROGEN AND PRESERVATIVE ELEMENTS TO WOOD

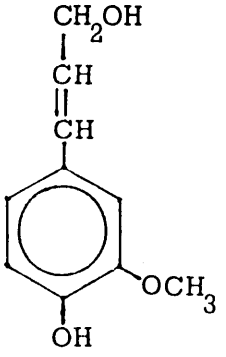
5.1 Introduction

Lignin is a major component of all woody tissue, generally comprising 16 to 24% (by weight) of hardwoods and 24 to 33% of softwoods (Sarkanen and Hergert, 1971). It is an amorphous, three-dimensional aromatic polymer composed of three oxyphenylpropane units: coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol (Fig 5.1). The relative proportions of these alcohols in lignin vary from one wood species to another. However, lignin found in wood can be divided into three broad categories: guaiacyl lignin, guaiacyl-syringyl lignin and guaiacyl-syringyl-p-hydroxyphenyl lignin.

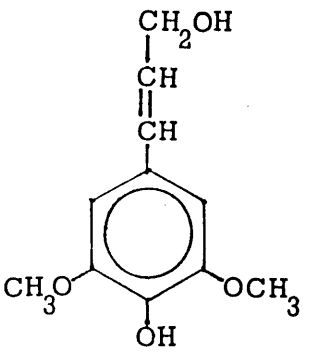
Guaiacyl lignin, found in most conifers (softwoods) is composed mostly of coniferyl alcohol with only small amounts of sinapyl and p-coumaryl alcohol. The proportion of coniferyl alcohol in spruce lignin may be more than 80% (Crawford, 1981). Guaiacyl-syringyl lignin, found in hardwoods and a few exceptional softwoods contains approximately equal amounts of coniferyl and sinapyl alcohols with only small amounts of p-coumaryl alcohol. Guaiacyl-syringyl-p-hydroxyphenyl lignin, found in the compression wood of conifers, contains approximately equal amounts of all three alcohols.

The oxyphenylpropane units which constitute lignin are synthesized in higher plants via the Shikimic acid pathway which is also responsible for the generation

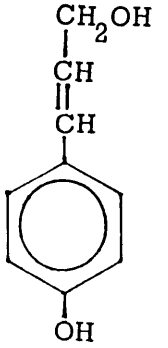
Fig 5.1 Chemical structures of the oxyphenylpropane precursors of lignin



Coniferyl alcohol



Sinapyl alcohol



P-coumaryl alcohol

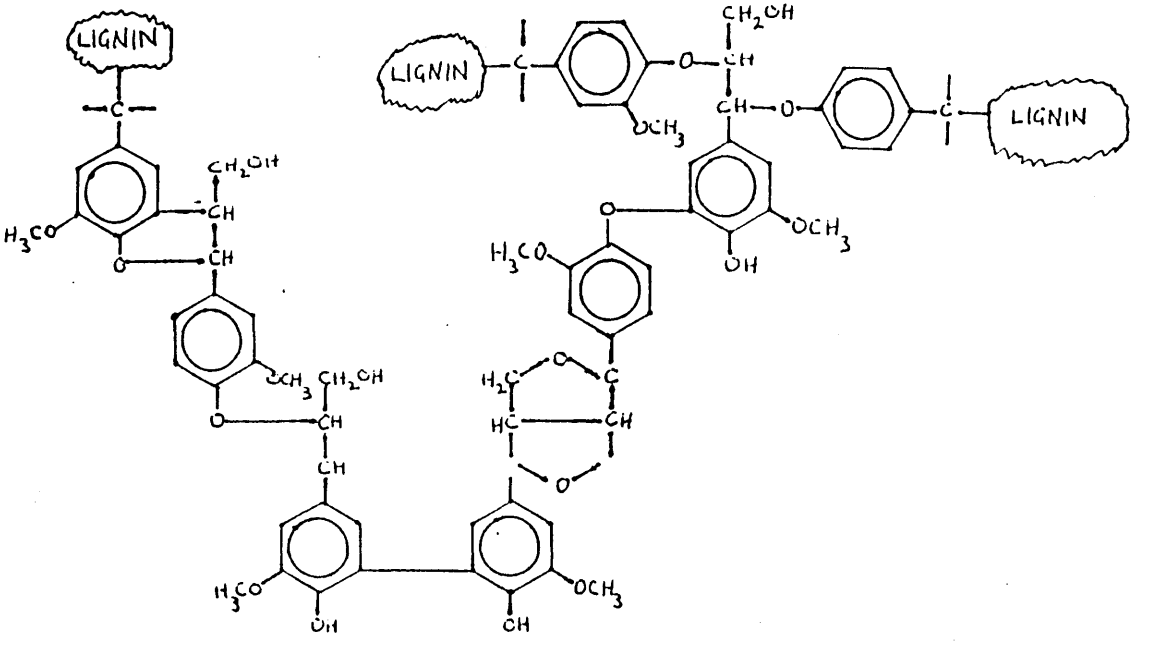
of many other aromatic compounds such as tryptophan, phenylalanine, tyrosine, cinnamic acids, alkaloids and other aromatic nitrogen compounds (Sarkanen, 1971). It is thought that some nitrogen from these other compounds may be incorporated into lignin with the oxyphenylpropane units.

Lignin is synthesized by polymerisation of the oxyphenylpropane units, mediated by phenyloxidase enzymes, probably peroxidases. The individual units become covalently linked to one another via -C-C- or -C-O-C- linkages as a result of dehydrogenation. The most important types of bonds between individual oxyphenylpropane units are shown in Fig 5.2, although other types of linkage are thought to exist.

Since it is composed of three different oxyphenylpropane monomers which can be linked in a variety of ways, lignin is a highly branched, structurally complex macromolecule. Such lignin found in wood may have a molecular weight of 100,000 or more (Goring, 1971).

The complex chemical structure of lignin, the aromatic nature of the oxyphenylpropane units from which it is formed and the stable nature of the covalent bonds between the units make lignin very resistant to microbial decay. The complete breakdown of polyaromatic molecules such as lignin, present in soil humus, may take several thousand years (Crawford, 1981). Therefore, in wood, lignin may

Fig 5.2 Structure of a hypothetical segment of conifer lignin



provide some protection to the more decay susceptible polysaccharides.

In vivo, lignin always exists in association with the polysaccharides cellulose and hemicellulose (for detail of the chemical structure of the polysaccharides, see Chapter 1). According to Côté (1977), cellulose, which provides tensile strength in the wood, forms a "framework" of microfibrils. Hemicellulose, which is formed at the same time as cellulose, provides a "matrix" around the cellulose which may provide some rigidity in the wood cell prior to lignification. During lignification, the precursors of lignin diffuse across the cell wall from the intercellular regions, starting at the cell corners. Polymerisation is then initiated and lignin is deposited around the cellulose microfibrils as an "encrusting" substance, which adds rigidity to the cell wall and renders it impermeable to water. The lignin may be associated with or chemically bound to the hemicellulose, forming an interpenetrating polymer complex which surrounds the cellulose microfibrils (Kirk, 1972).

Studies of the ultrastructure of wood cell walls, (Côté, 1977) using scanning electron micrographs of wood delignified using chlorite and of lignin skeletons prepared by treatment of wood with hydrofluoric acid, reveal that the polysaccharide and lignin components are distributed right across the cell wall. However, in

both hardwood fibres and softwood tracheids, the highest density of lignin is in the middle lamella region between wood cells, most particularly at the cell corners and in the primary cell wall. The secondary cell wall contains a much lower density of lignin and consequently a higher proportion of polysaccharide, although the S_1 and S_3 layers are thought to contain more lignin than the much thicker S_2 layer that lies between them.

Since lignin is present in all layers of the wood cell walls, it may act as a physical or chemical barrier to the decay of the polysaccharides cellulose and hemicellulose which it encrusts. A high density of lignin in the S_3 layer may be particularly important in preventing penetration of micro-organisms from the cell lumen into the cellulose-rich S_2 layer. Butcher and Nilsson (1982) found a good correlation between the lignin contents of various species of hardwood and their decay susceptibility: wood species with a high lignin content were more resistant to fungal decay. Holt and Jones (1978) demonstrated degradation of both a hardwood and a softwood by the bacterium *Cellvibrio vulgaris* only after partial delignification of the wood. Zainal (1975) studied the effect of delignification on the decay of pine and birch by the soft-rot fungus *Phialophora fastigiata*. The removal of lignin from blocks of both species resulted in much higher weight losses after six weeks exposure to the fungus. In addition, the cavities in the S_2 layer

normally associated with soft-rot attack were absent from delignified pine and the individual layers of the cell wall became indistinguishable. Thus the presence of lignin clearly restricts the activity of soft-rot fungi either by acting as a physical barrier to the penetration of hyphae into the cellulose microfibrils or by restricting the action of the enzyme system of the fungus, or possibly a combination of both. Lignin should not prove such a barrier to either the white-rotting or the brown-rotting Basidiomycete fungi, but since these fungi are generally inhibited by the presence of wood preservatives in timber in service, the resistance of lignin to soft-rot decay could be an important factor in the durability of preservative treated wood in soil contact situations.

Lignin may also play an important role in the fixation of heavy metal preservatives to wood by providing complexing and cation exchange sites and may therefore determine both the mode of action and performance of preservatives in wood in service.

The oxyphenylpropane units which make up lignin (Fig 5.1) all contain both methoxyl (OCH_3) and phenolic (OH) groups attached to the aromatic ring which may act as potential complexing and cation exchange fixation sites respectively for heavy metal ions in preservative solutions. Many of the phenolic groups are converted to ester linkages with the side chains of adjacent alcohol units during

polymerisation, such ester linkages being the commonest type of linkage found in lignin (Kirk, 1972). However, natural lignin in wood must still contain large numbers of both methoxyl and phenol groups which should be available as fixation sites for preservative elements.

Cellulose, in its pure form, possesses none of the polar groups present in lignin and its role in the complexing and cation exchange fixation of heavy metals must therefore be more limited. However, oxidation of cellulose within the wood may lead to the production of carboxyl groups which could act as cation exchange sites. Studies on the absorption of copper from solutions by α cellulose (Belford, Preston, Cook and Nevard, 1957; Belford, Myers and Preston, 1958; Michie, 1961) suggest that copper ions are adsorbed onto the surface of cellulose microfibrils in an ordered fashion, possibly becoming fixed onto hydroxyl or carboxyl groups. However, these studies were carried out in the absence of lignin which, in normal wood, would be expected to compete with cellulose for cations.

Bland (1963) found that absorption of copper from copper acetate solution was 8 times greater in milled wood lignin than in α cellulose, whilst in an identical experiment using normal wood, most of the copper was taken up by the primary wall and middle lamella region of wood cells, where most of the cell wall lignin is located.

This study appears to confirm that the lignin component of wood is most important in complexing and cation exchange fixation of heavy metals.

Hemicellulose may also provide some suitable sites for complexing or cation exchange fixation of preservative elements in the form of acetone, carboxyl and methoxyl groups attached to side chains. However, since hemicellulose cannot readily be isolated from wood in the absence of cellulose, its role in preservative fixation is uncertain.

In CCA treated wood, some of the copper and chromium, in the form of copper (II) and chromium (III) ions, are thought to become complexed or fixed by cation exchange mechanisms to functional groups in the wood (Dahlgren and Hartford, 1972a; b; c; Pizzi, 1982c), probably primarily on lignin. The oxidation of the lignin and polysaccharide components of the wood by chromium (VI) present in the CCA treating solution would greatly increase the number of carboxyl groups present in wood, providing further sites for complexing and cation exchange fixation. In addition, Pizzi (1982a; b; c) proposed that chromium (VI) complexes with lignin, forming chromate bridges linking four adjacent coniferyl alcohol groups. However, precipitation reactions forming copper (II) and chromium (III) arsenates and copper chromate are also thought to be an important aspect of the fixation of CCA to wood (Dahlgren and Hartford, 1972a; b; c; Pizzi, 1982c). Such

precipitated CCA deposited in the S_2 layers of wood cells might be most important in preventing soft-rot decay.

Sub-microscopic studies on the microdistribution of preservative elements in the tracheids of pine wood treated with CCA (Chou, Chandler and Preston, 1973) revealed that, with the exception of occasional "coarse" deposits thought to be mostly copper, most preservative elements in the S_2 layer appeared to be associated with the surface of the cellulose microfibrils, either attached directly to the cellulose or to the encrusting lignin and hemicellulose deposits. Therefore, even the insoluble copper (II) and chromium (III) arsenates and hydroxides and copper chromate may be complexed to the wood constituents rather than simply being deposited in the cell wall and Pizzi (1982c) proposed that lignin would be the main site for such complexing reactions.

The role of lignin-bound CCA in protecting the polysaccharide components of wood against soft-rot attack is unclear. Toxic elements bound to lignin could only be directly toxic to micro-organisms if they were released into solution. This condition could be met for cation exchange fixed copper (II) and chromium (III) ions in moist CCA treated wood in soil contact where some exchange of these ions with the soil solution, and hence with the soil itself, would be expected. Secretions from metabolising fungi have been shown to cause solubilisation of preservative

elements from CCA treated wood (Levi, 1969) and such secretions might be particularly active in the release of cation exchange fixed toxic elements during decay, with the solubilised preservative being absorbed by fungal hyphae (Chou, Preston and Levi, 1973).

CCA bound to lignin encrusting cellulose microfibrils might also act as a physical barrier to the penetration of soft-rot microfungi into the cellulose, especially if the cellulolytic enzymes of the fungi are membrane-bound.

Chou, Chandler and Preston (*op cit*) observed a deposit of preservative elements covering the lumen surface of the comparatively lignin-rich S_3 layer of tracheids in CCA treated pine. CCA bound to lignin in the S_3 layer of wood cells might be particularly important in protecting the polysaccharide-rich S_2 layer, since penetration of fungal hyphae into the cell normally occurs from the lumen via the S_3 layer. Nilsson (1982) postulated that lignin-bound copper in the S_3 layer might mask "t-branch initiation sites" necessary for fungi to penetrate into the S_2 layer.

In ACA treated wood, much of the copper, probably in the form of cuprammonium ions, is thought to become fixed to wood by cation exchange or complexing mechanisms (Hulme, 1979). Again, this type of fixation reaction would be expected to occur mostly with the lignin component

of the wood and it can be postulated that such lignin-bound copper in ACA treated wood might have a similar mode of action against micro-organisms as lignin-bound copper and chromium in CCA treated wood. In ACA treated wood, some ammonium ions would also be expected to become fixed to cation exchange sites on lignin, possibly providing a store of nitrogen available as a nutrient to micro-organisms in the wood and thus increasing the wood's susceptibility to decay (Chapter 4).

The cation exchange capacity of lignin may also be important in determining the decay of preservative treated and untreated timber in soil contact, since cations such as potassium, calcium, magnesium and ammonium ions, found in soil, may become bound to lignin. High concentrations of potassium, magnesium and calcium ions in solution have been shown to increase the leachability of copper from CCA treated wood (Plackett, 1984) and the most likely explanation of this effect is that the cations compete with and displace copper ions from cation exchange sites on the wood. Thus, high concentrations of inorganic metallic salts in solution should cause increased copper losses from CCA treated wood in soil. Also, cationic nutrients present in soil, particularly ammonium ions, which become bound to lignin, may provide a readily available source of nutrients to micro-organisms invading the wood.

Studies on forest litter biodeterioration (Berg, 1978; Berg and Staaf, 1980) have shown that much of the nitrogen which accumulates in the litter during decomposition becomes bound to lignin. Berg (1978) found that the percentage of total nitrogen in the litter bound to lignin increased steadily during decay until the lignin started to be depleted. Beyond this point, the percentage of lignin-bound nitrogen remained constant at about 50%. Berg and Staaf (1980) attributed this increase in lignin nitrogen content to nitrogen being mineralised during decomposition and becoming bound to lignin. Studies on wood blocks buried in soil (Kane, 1981; King, Mowe, Bruce and Smith, 1983) confirmed that nitrogen accumulated on the lignin fraction of wood during the early stages of decay, in a manner similar to that observed for forest litter. However, Kane found that, in lime blocks, as decay became more severe, there was a subsequent fall in lignin nitrogen content, despite a continued rise in total wood nitrogen content. Since wood has a much lower nitrogen content than most other plant litter (Merrill and Cowling, 1966), the nitrogen accumulated on wood lignin during decay is most likely to be of a microbial origin rather than from the mineralisation of wood nitrogen.

In both wood and forest litter, nitrogen accumulated on lignin during decomposition would most probably be in the form of aqueous ammonia, ammonium ions or amino acids

fixed to lignin by cation exchange mechanisms, or by condensation reactions leading to direct covalent bonding (or a combination of both). Ammonium ions and amino acids are readily utilisable by micro-organisms as nitrogen sources and lignin-bound nitrogen, in the form of these compounds, may therefore be important in the decay processes of both wood in soil and forest litter. Such nitrogen sources fixed to cation exchange sites on lignin would be released into decaying wood in response to a fall in the concentration of available soluble nitrogen in the wood. Nitrogen bound more permanently to lignin would also be released during the later stages of decay when the lignin was being degraded. Thus, lignin nitrogen could maintain the availability of this decay-limiting nutrient to micro-organisms and therefore assist in the decay process. The observed fall in the lignin nitrogen content of wood during the later stages of decay (Kane, *op cit*) suggests that nitrogen was indeed being released into the wood, where it would quickly be assimilated by micro-organisms.

Therefore, lignin may play a fundamental part in determining the performance of preservative treated and untreated wood in soil contact, both in the fixation of preservative elements and in maintaining the availability of nutrients, especially nitrogen.

The current studies

This chapter describes experiments undertaken to study aspects of the role of lignin in the fixation of both nitrogen and preservative elements to wood and changes in the amounts of nitrogen and preservative elements bound to lignin during burial of wood in soil.

Firstly, lignin was isolated from untreated and ACA treated blocks of pine set aside from the ACA burial experiment (Chapter 4). Nitrogen and copper contents were determined for the lignin fractions of these blocks and thus the role of lignin in the fixation of copper and nitrogen to wood was studied and changes in lignin nitrogen and copper contents during the decay process were monitored. Pine alone was used in this experiment and only one ACA treatment level was used as a result of time limitations. The treating concentration chosen was selected to show some limited decay of the treated blocks during the 18 week burial period.

Secondly, CCA treated blocks of normal wood, extracted wood lignin and extracted wood holocellulose were subjected to an aqueous leaching programme in order to determine the role of lignin in the fixation of CCA to these wood components.

The role of lignin in the above processes may be studied using two different approaches: firstly, lignin

can be isolated from wood by removing the polysaccharides by chemical means; secondly, wood can be chemically delignified and the properties of wood studied in the absence of lignin. Both approaches were used in these studies.

Isolation of lignin

Lignin can be isolated from wood by many different methods and the isolation procedures can be classified into three basic types: isolation by extraction, isolation as a residue and isolation as derivatives. Lignin isolated by extraction is dissolved in organic solvents which do not react with it. However, only a small fraction of the total lignin is soluble in solvents and, after purification, forms a solid known as "native lignin". The proportion of lignin soluble in solvents can be increased by milling the wood (milled wood lignin) or by attack of the wood with brown-rot fungi (enzymatically liberated lignin) prior to extraction. However, neither of these methods extract all of the lignin from the wood. Lignin can be isolated as a residue by removing the polysaccharides from the extractive-free wood by means of acid hydrolysis, oxidation by periodate or solution in cuprammonium hydroxide. The lignin remains as a solid residue. Lignin can be isolated as derivatives by treating wood with reagents that react with lignin to form soluble products. These can then be separated from polysaccharides

through solubility or chemical behaviour, although yields of lignin are not quantitative.

In the present studies, determination of lignin nitrogen required that all lignin had to be recovered quantitatively from the wood. Therefore, for lignin nitrogen determinations, only procedures isolating lignin as a residue were suitable. For the purposes of the CCA leaching study, it was hoped to retain the lignin in the form of blocks. This could also only be achieved by isolating the lignin as a residue.

Lignin can be isolated as a residue by hydrolysis of the polysaccharides in extractive-free wood by strong mineral acids, normally sulphuric acid (producing Klason lignin) or hydrochloric acid (producing hydrochloric acid lignin). Although the sulphuric acid Klason technique is recognised as the standard procedure for determining lignin in wood (Tappi standard T13m-54), lignin isolated by means of mineral acids undergoes condensation reaction both between adjacent oxyphenylpropane units and between lignin and other compounds such as proteins and polyphenols (Lai and Sarkanen, 1971). These reactions drastically alter the chemical properties of the lignin and any condensation of protein would interfere with the determination of lignin nitrogen. In addition, the very low pH involved in acid hydrolysis of polysaccharides would be expected to cause the solubilisation of preservative

elements and nitrogen compounds fixed to lignin by cation exchange mechanisms. Thus, isolation of lignin by acid hydrolysis was not entirely suitable for the present studies.

Cuprammonium lignin is prepared by alternate hydrolysis with dilute boiling sulphuric acid and treatment with cuprammonium solution. Although the lignin is isolated as a residue, the yield is low since some of the lignin is rendered soluble by the treatment. Also, the copper and ammonia used in the procedure could interfere in lignin copper and nitrogen determinations, making the procedure totally unsuitable for the present studies.

Lignin can also be isolated as a residue by treatment of extractive-free wood with periodate (tri-sodium dihydrogen orthoperiodate) at pH 4 (Ritchie and Purves, 1947). Individual sugar units of the polysaccharides, oxidatively cleaved by the periodate, are hydrolysed with boiling water, leaving all of the wood lignin as an insoluble residue known as "periodate lignin". This preparation retains the original structure of lignin and also avoids the condensation reactions which occur during acid hydrolysis of wood. However, some oxidation of the oxyphenylpropane units, especially free phenolic groups, may occur (Lai and Sarkanen, 1971). Despite such oxidation, periodate lignin is the least modified form of lignin which can be isolated as a residue and this procedure

was therefore selected for preparing lignin in both experiments described in this chapter.

Wood to be treated with periodate must be pre-extracted with solvents to remove extractives and a small portion of soluble lignin. The most commonly used extraction procedure uses a four hour Soxhlet extraction with 95% ethanol followed by a further four hour Soxhlet extraction with a 1/1 $\frac{v}{v}$ mixture of 95% ethanol and benzene. This latter mixture can be replaced by a 2/1 $\frac{v}{v}$ mixture of ethanol/toluene to avoid the use of the more toxic benzene. Freudenberg and Neish (1968), however, recommended the use of a 9/1 $\frac{v}{v}$ mixture of acetone/water at room temperature to replace the Soxhlet extraction procedure. This latter extraction procedure was adopted for the pre-extraction of wood before periodate treatment.

The isolation of lignin by the periodate procedure requires several successive treatments of the wood with periodate solution, each followed by thorough washing and boiling of the preparation under reflux. The refluxing step is intended to bring about the hydrolysis of carbohydrates oxidised by the periodate. In the present study, the refluxing was replaced by Soxhlet extraction of the preparation with hot water since this less severe process also achieved the required hydrolysis and removal of the carbohydrate (Section 5.2.3.2).

Delignification of wood blocks

Wood is most commonly delignified by treatment with either chlorine or chlorine dioxide, either in gaseous form or in solution, forming "holocellulose", which retains both the cellulose and hemicellulose fractions of the original wood. The action of chlorine and chlorine dioxide may cause some oxidation and breakdown of the polysaccharides, although the use of chlorine dioxide is thought to preserve more of the hemicelluloses.

The most convenient method of delignifying wood with chlorine dioxide is by means of the acid chlorite procedure (Wise, Murphy and D'Addieco, 1946): the wood is subjected to successive treatment with an acidified solution of sodium chlorite which decomposes to form chlorine dioxide.

$$5ClO_2^- + 2H^+ \longrightarrow 4ClO_2 + Cl^- + 2OH^-$$

Although complete delignification cannot be achieved without excessive loss of polysaccharide, allowing a few percent of lignin to remain in the holocellulose preparation offsets this problem (Browning, 1967).

Zainal (1975) delignified whole wood blocks using acid chlorite solution buffered at pH 4.7. The temperature was maintained at 75°C and the solution changed hourly. This procedure was adopted for the preparation of whole blocks of holocellulose for the present studies.

Both periodate lignin and acid chlorite holocellulose blocks prepared for use in the present studies were analysed for Klason lignin content following the Tappi standard method (T13m-54) to ensure that the polysaccharides and lignin respectively had been successfully removed from the blocks. For these Klason determinations, the ethanol and ethanol/toluene Soxhlet pre-extraction procedure specified in the standard was used.

Aims of the present studies

The experimental work described in this chapter fell into two sections outlined previously.

The aims of the first experiment were to:

1. determine the amount of lignin-bound nitrogen and copper in untreated and ACA treated pine blocks following impregnation and curing

2. determine any changes in lignin nitrogen and copper contents of these blocks during soil burial

3. determine the percentage of total wood nitrogen and copper in the above blocks bound to the lignin fraction both prior to and during soil burial.

The aims of the second experiment were to:

1. determine selective absorption ratios for all preservative elements in normal wood, holocellulose and periodate lignin blocks of lime and pine after impregnation with a 3% $\frac{W}{V}$ CCA solution

2. determine percentage losses of preservative elements from CCA treated normal wood, holocellulose and periodate lignin blocks of lime and pine during aqueous leaching

3. determine atom ratios for the preservative elements in the above blocks both after treatment with CCA solution and after aqueous leaching.

5.2 Materials and Methods

5.2.1 Preparation of wood blocks

Centre wood blocks (10 x 10 x 5 mm) with large radial faces (10 x 10 mm) were prepared from the sapwood region of oven dried planks of the hardwood lime (*Tilia vulgaris*, Hayne) and the softwood pine (*Pinus sylvestris*, L) as described in Chapter 2.

The blocks were labelled, oven-dried at 102°C for 3 hours and individually weighed.

5.2.2 Acid chlorite delignification procedure (Zainal, 1975)

5.2.2.1 Preparation of the acid chlorite solution

Sodium chlorite (33 g), sodium acetate (41 g) and glacial acetic acid (30 g) were dissolved in distilled water and made up to 1 litre. The pH of this buffered solution was 4.7. Fresh solution was prepared for each delignification treatment.

5.2.2.2 Delignification procedure

Thirty centre wood blocks of lime (total mass approximately 9 g), prepared as described above, were placed in a beaker in a vacuum dessicator. A vacuum was drawn for 15 minutes and 250 cm^3 acid chlorite solution was then introduced to the beaker. The vacuum was

released and the beaker covered and transferred to a water bath at 75°C for 6 hours. The acid chlorite solution was replaced by 250 cm^3 fresh solution every hour.

After 6 hours, the beaker was removed from the water bath and its contents were allowed to stand at room temperature overnight. The acid chlorite solution was then replaced with fresh solution and the beaker returned to the water bath for a further 6 hours. Again, the acid chlorite solution was replaced every hour.

The blocks were then removed from the chlorite solution and washed thoroughly with distilled water. They were placed on paper tissue in a vacuum dessicator and a vacuum drawn for 15 minutes to remove excess liquid. The blocks were then allowed to stand in 500 cm^3 distilled water overnight and subsequently washed twice more in distilled water. A final vacuum was applied to remove excess liquid from the blocks and they were then oven-dried at 102°C for 3 hours and re-labelled.

Five of the oven-dried blocks were weighed and their mean percentage weight loss calculated. The whole acid chlorite/washing treatment of the blocks was then repeated a further three times and the percentage weight loss of five blocks was calculated after each treatment.

30 centre wood blocks of pine (see Section 5.2.1) were also delignified as described above.

5.2.2.3 Weight loss of blocks during delignification

The mean percentage weight loss values (± standard deviations) for the five blocks of lime and five blocks of pine weighed after each chlorite treatment are shown in Table 5.1.

Table 5.1

Mean percentage weight loss (± standard deviations) of lime and pine blocks during acid chlorite delignification

Number of acid chlorite treatments	% Weight Loss (± Standard Deviations)	
	Lime	Pine
1	8.74 ± 1.03	9.42 ± 1.50
2	15.15 ± 0.95	13.45 ± 1.87
3	17.54 ± 1.25	22.85 ± 1.40
4	20.13 ± 0.42	25.09 ± 0.50

For both lime and pine blocks, the percentage weight loss increased with each successive acid chlorite treatment up to 20.13 and 25.09% weight loss for lime and pine blocks respectively after four treatments. These values are close to the normal lignin contents for lime and pine. Further chlorite treatments were therefore not undertaken in order to avoid excessive loss of polysaccharides which may occur if delignification with acid chlorite solution is

continued in an attempt to remove every trace of lignin (Browning, 1967).

5.2.3 Preparation of periodate lignin (Ritchie and Purves, 1947)

5.2.3.1 Preparation of the periodate solution

A 4.5% $\frac{W}{V}$ solution of tri-sodium dihydrogen orthoperiodate was prepared as follows: 45 g of tri-sodium dihydrogen orthoperiodate ($Na_3H_2IO_6$) was added to 600 cm^3 distilled water on a magnetic stirrer. Glacial acetic acid was gradually added until the solution cleared. A pH electrode was then placed in the solution and further glacial acetic acid added dropwise until the pH fell to 4.1. The solution was then transferred to a 1 litre volumetric flask and made up to the mark with distilled water.

5.2.3.2 Treatment of wood with periodate

The procedure described is a modification of the method of Ritchie and Purves (1947).

In the original method of Ritchie and Purves, wood meal was boiled in water under reflux to remove carbohydrate oxidised during the periodate treatment. However, in the present study, the wood was required to remain in the form of whole blocks. Therefore, a hot water Soxhlet extraction was used to extract the carbohydrate from the

blocks in order to minimise disturbance of the blocks.

Principle

Whole blocks were pre-extracted with an acetone: water solution (9:1 by volume) at room temperature (about 20°C) for 6 hours, washed in distilled water and oven-dried at 102°C for 3 hours. The blocks were then treated with periodate solution on a magnetic stirrer for 24 hours at room temperature, percolated with cold water for 4 hours, extracted with water in a Soxhlet apparatus for 4 hours, washed again with distilled water and oven-dried at 102°C for 3 hours. The blocks were subjected to the whole periodate/water treatment six times and were weighed after each treatment to determine the percentage weight loss.

Procedure

48 oven-dried centre wood blocks of lime (see Section 4.2.1) were separated into 3 groups of 16 blocks. A total dry weight was obtained for each set of blocks. Each group of blocks was transferred to a separate sintaglass extraction thimble (porosity 1). An acetone/ water solution (9:1 by volume) at room temperature (about 20°C) was then run over the blocks from a separating funnel, adjusting the flow so that the liquid in the extraction thimble just covered the blocks. The blocks

were thus extracted for 6 hours, rinsed thoroughly with distilled water and then oven-dried at 102°C for 3 hours. The extractive-free dry weight of each set of blocks was then determined.

Each set of blocks was transferred to a separate 250 cm^3 beaker and placed in a vacuum dessicator. A vacuum was drawn for 15 minutes and 100 cm^3 of the periodate solution was then introduced to each beaker and the vacuum released. The beakers were covered and placed on magnetic stirrers for 24 hours at room temperature. An asbestos mat was placed underneath each beaker to prevent heat from the stirrer motor raising the solution temperature above room temperature.

After the periodate treatments, the blocks were returned to the extraction thimbles and percolated with distilled water at room temperature for 4 hours in the same manner as for the acetone/water pre-extraction. The extraction thimbles were then transferred to Soxhlet apparatus and the blocks extracted with hot water for a further 4 hours. The blocks were then rinsed thoroughly with distilled water, oven-dried at 102°C for 3 hours and a new dry weight was determined for each set of blocks.

The whole periodate/water treatment was repeated a further five times and the dry weight of each group of blocks was determined after each treatment and the percentage weight loss calculated.

48 centre wood blocks of pine (see Section 5.2.1) were also treated as described above.

5.2.3.3 Weight loss of blocks during periodate treatment

The mean percentage weight loss (± standard deviations) for the three groups of lime blocks and three groups of pine blocks after pre-extraction and after each periodate treatment are shown in Table 5.2. All weight losses are expressed as percentages of the original unextracted dry weights of blocks.

Table 5.2

Mean percentage weight loss (± standard deviations) of lime and pine blocks during acetone/water pre-extraction and during treatment with periodate

Treatment		% Weight Loss (± Standard Deviations)	
		Lime	Pine
Acetone/water pre-extraction		3.54 ± 0.08	1.33 ± 0.15
Periodate Treatment	1	20.64 ± 2.12	24.95 ± 0.81
	2	33.50 ± 2.67	44.39 ± 4.42
	3	59.88 ± 3.29	56.53 ± 2.42
	4	63.57 ± 1.75	61.85 ± 5.45
	5	74.39 ± 2.29	68.68 ± 0.99
	6	80.00 ± 0.91	73.01 ± 1.81

For both lime and pine blocks, weight loss during pre-extraction with acetone/water was small (3.54% and 1.33% for lime and pine respectively). Weight losses of blocks of both wood types increased with successive periodate treatments, reaching 80% for lime blocks and 73% for pine blocks after six treatments. Therefore, hot water extraction in Soxhlet apparatus was clearly as effective as boiling under reflux at removing cellulose oxidised by the periodate from the wood.

The percentage of the original wood remaining after six periodate treatments was 20% for lime and 27% for pine. These values are close to the normal lignin contents of the two wood types and therefore further periodate treatments were not undertaken in order to avoid excessive oxidation of the lignin isolated.

5.2.4 Klason lignin determinations

Delignified and periodate lignin blocks of lime and pine, prepared as described above, were analysed for percentage lignin content by the Klason method (Tappi standard T13M-54). Untreated blocks of lime and pine were also analysed for lignin content using the same procedure.

5.2.4.1 Preparation of 72% sulphuric acid

665 cm^3 concentrated H_2SO_4 was added to 300 cm^3 distilled water and allowed to cool. The mixture was transferred to a 1 litre volumetric flask and made up to the mark.

The molarity of the acid was determined by titration against standard 0.1M NaOH. The molarity was adjusted to 12M by a further small addition of concentrated H_2SO_4.

5.2.4.2 Procedure

Approximately 1 g of wood sample was prepared by chopping blocks into small splinters using a sharp scalpel. The sample was oven dried at 102°C for 3 hours, weighed and then transferred to a sintered glass extraction thimble.

The sample was extracted for 4 hours in a Soxhlet apparatus using 95% ethanol. The excess solvent was then sucked out using a Büchner funnel attached to a water pump. The sample was returned to the Soxhlet apparatus and extracted for 4 hours using a mixture of 2 parts toluene : 1 part 95% ethanol. Excess solvent was again sucked out and the sample was washed with 50 cm^3 ethanol.

The sample was allowed to air-dry and was then transferred to a 50 cm^3 beaker with a watch glass cover. 15 cm^3 72% sulphuric acid at 12 - 15°C was slowly added to the sample with stirring and the beaker was transferred to a water bath maintained at 18 - 20°C and allowed to stand for 2 hours. The contents of the beaker were stirred frequently.

The residue was washed into a 1 litre conical flask and the acid diluted to 3% using 560 cm^3 distilled water. The contents of the conical flask were then boiled under reflux for 4 hours and were subsequently allowed to cool and settle. The residue was then filtered into an oven-dried, weighed extraction thimble on a Büchner flask, washed with distilled water, oven-dried at 102°C for 3 hours and then re-weighed.

The dry weight of the residue was expressed as a percentage of the initial dry weight of the sample.

The above procedure was performed in triplicate on normal, delignified and periodate lignin blocks of both lime and pine.

5.2.4.3 Klason lignin contents of normal, delignified and periodate blocks

The percentage Klason lignin contents (± standard deviations) of normal, delignified and periodate blocks of lime and pine are presented in Table 5.3.

Table 5.3

Percentage Klason lignin contents (± Standard Deviations) of normal, delignified and periodate blocks of lime and pine

Wood Type	Percentage Klason Lignin Content
Normal Lime	18.62 ± 0.57
Delignified Lime	1.83 ± 0.46
Periodate Lime	78.75 ± 4.80
Normal Pine	25.40 ± 0.58
Delignified Pine	1.91 ± 0.34
Periodate Pine	90.08 ± 0.14

The Klason lignin contents of normal wood blocks, being 18.6 and 25.4% for lime and pine respectively, are somewhat lower than the lignin contents obtained using the periodate method but conformed closely to the expected values for the two wood types.

Klason determinations on the delignified wood blocks confirmed that a small amount of lignin (about 2% by weight) was retained in both lime and pine blocks after delignification.

Klason lignin determinations on the periodate lignin preparations showed that a portion of the periodate lignin was soluble in 72% H_2SO_4. 90% of pine periodate lignin

remained after Klason determination but only 78.75% of periodate lignin from the hardwood lime remained after the same treatment. Ritchie and Purves (1947) similarly obtained higher yields of Klason lignin from softwood periodate lignin than from periodate lignin isolated from hardwoods.

5.2.5 Studies on lignin nitrogen and copper in untreated and ACA treated pine during soil burial

In the ACA soil burial experiment (Chapter 4), a total of fifteen untreated pine blocks and fifteen pine blocks treated with 0.071% $\frac{W}{V}$ ACA were buried in soil for exhumation at each sampling interval (6, 12 and 18 weeks). A further fifteen blocks of each type were included as unburied control blocks.

All exhumed blocks were weighed wet, oven-dried at 102°C for 3 hours, re-weighed and their percentage moisture contents and weight losses calculated (see Chapter 4, Section 4.2.6).

Five untreated and five 0.071% $\frac{W}{V}$ ACA treated blocks at each sampling interval were analysed for % $\frac{W}{W}$ ammonium nitrogen, total nitrogen and copper contents as part of the ACA burial study and the results of these analyses were presented in Chapter 4. The percentage weight losses of these blocks were also presented in Chapter 4.

The remaining ten untreated and ten 0.071% $\frac{w}{v}$ ACA treated blocks at each sampling interval (including unburied controls) were used in the present study. Their percentage weight losses are presented in the results section of this chapter. Each set of ten blocks was treated with periodate solution to isolate periodate lignin. The lignin fractions isolated from each set of ten blocks were subsequently analysed for % $\frac{w}{w}$ nitrogen and copper contents.

5.2.5.1 Isolation of periodate lignin from blocks

All blocks were cut into small sticks with a sharp scalpel and the sticks produced from the ten untreated or ACA treated blocks at each sampling interval were combined together and placed in a separate sintaglass extraction thimble.

The sticks contained within each extraction thimble were then pre-extracted with acetone/water and given six periodate/water treatments following the procedure described in Section 5.2.3.2. The residual dry weight of each sample was determined after acetone/water pre-extraction and after each periodate/water treatment.

5.2.5.2 Nitrogen and copper analysis of periodate lignin

The lignin residue from each set of ten blocks, prepared as described above, was split into three equal portions and their dry weights were determined.

The three portions were digested individually in concentrated H_2SO_4 and "100 volume" H_2O_2 and analysed for % $\frac{W}{W}$ nitrogen by a micro-Kjeldahl technique (Chapter 2, Section 2.2.7). The digest was recovered from the distillation apparatus, re-acidified and then analysed for % $\frac{W}{W}$ copper on an A.A.S. by a standard additions technique (Chapter 2, Section 2.2.7.3).

From the analyses of the individual portions, mean % $\frac{W}{W}$ nitrogen and copper contents (± standard deviations) were calculated for the lignin fractions of both untreated and ACA treated pine blocks at each sampling interval. These values were then compared with the % $\frac{W}{W}$ nitrogen and copper contents of whole blocks, obtained from the main ACA burial experiment. Proportions of total wood nitrogen and copper on lignin and changes in these proportions during soil burial were calculated.

5.2.5.3 Calculations

In order to illustrate the calculations undertaken a worked example is described. The example used is 0.071% $\frac{W}{V}$ ACA treated pine blocks exhumed at the 18 week sampling interval.

1. Percentage periodate lignin content of blocks was calculated, expressed as a percentage of the pre-burial dry weight of the wood:

$$\% \text{ Periodate lignin} = \frac{\text{dry wt. of periodate lignin residue from 10 blocks}}{\text{Pre-burial dry wt. of 10 wood blocks}} \times 100$$

For 0.071% $\frac{W}{V}$ ACA treated pine blocks at 18 weeks:

$$\% \text{ periodate lignin content} = \frac{0.5021}{2.0494} \times 100 = 24.5\%$$

2. The number of milligrams of nitrogen and copper per gram of whole wood blocks were calculated:

$$\text{mg nitrogen or copper per g of wood} = \% \frac{W}{W} \text{ N or Cu in wood blocks} \times 10$$

For 0.071% $\frac{W}{V}$ ACA treated pine blocks at 18 weeks:

mg nitrogen/g wood = 0.264 x 10 = 2.64 mg N/g wood

mg copper/g wood = 0.070 x 10 = 0.70 mg Cu/g wood

3. The number of milligrams of nitrogen and copper per gram of periodate lignin were calculated:

$$\text{mg nitrogen or copper per g periodate lignin} = \% \frac{W}{W} \text{ N or Cu in lignin fraction} \times 10$$

For 0.071% $\frac{W}{V}$ ACA treated pine blocks at 18 weeks:

mg nitrogen/g lignin = 0.535 x 10 = 5.35 mg N/g lignin

mg copper/g lignin = 0.018 x 10 = 0.18 mg Cu/g lignin

4. The number of milligrams of lignin bound nitrogen and copper per gram of wood were calculated:

$$\text{mg lignin N or Cu/g wood} = \text{Mg N or Cu/g lignin (from 3)} \times \frac{\% \text{ lignin content}}{100}$$

For 0.071% $\frac{w}{v}$ ACA treated pine blocks at 18 weeks:

$$\text{mg lignin N /g wood} = 5.35 \times \frac{24.5}{100} = 1.311 \text{ mg lignin N/g wood}$$

$$\text{mg lignin Cu /g wood} = 0.18 \times \frac{24.5}{100} = 0.044 \text{ mg lignin Cu/g wood}$$

5. The amount of lignin bound nitrogen and copper (in milligrams) was expressed as a percentage of total wood nitrogen or copper (in milligrams):

$$\text{\% of total wood N or Cu bound to lignin} = \frac{\text{mg lignin N or Cu/g wood (from 4)}}{\text{Mg N or Cu/g wood (from 2)}} \times 100$$

For 0.071% $\frac{w}{v}$ ACA treated pine blocks at 18 weeks:

$$\text{\% of total wood N bound to lignin} = \frac{1.311}{2.64} \times 100 = 49.66\%$$

$$\text{\% of total wood Cu bound to lignin} = \frac{0.044}{0.70} \times 100 = 6.29\%$$

The same calculations were also undertaken on the data from all other sets of blocks.

6. Percentage periodate lignin content was also calculated, expressed as a percentage of the extractive-free dry mass of wood after exhumation from soil.

$$\text{\% periodate lignin} = \frac{\text{dry wt. of periodate lignin residue from 10 blocks}}{\text{dry wt. of exhumed blocks after acetone/water extraction}} \times 100$$

For 0.071% $\frac{w}{v}$ ACA treated pine blocks at 18 weeks:

$$\text{\% periodate lignin} = \frac{0.5021}{1.8646} \times 100 = 26.9\%$$

5.2.6 Leaching studies on CCA treated periodate lignin, holocellulose and normal wood

Normal, delignified (holocellulose) and periodate lignin blocks of both lime and pine were impregnated with a 3% $\frac{w}{v}$ CCA solution and cured. The blocks were then leached in groups of five for 6 days in distilled water. Both blocks and leachates were analysed for copper, chromium and arsenic.

5.2.6.1 Preparation of blocks

The numbers of blocks of each wood type prepared are shown in Table 5.4.

Table 5.4

Numbers of normal, delignified and periodate lime and pine blocks prepared

Wood Type	Number of blocks prepared
Normal Lime	25
Delignified Lime	25
Periodate Lime	30
Normal Pine	25
Delignified Pine	25
Periodate Pine	30

Normal centre wood blocks of lime and pine were prepared as described in Section 5.2.1.

Delignified blocks of both lime and pine were prepared following the acid chlorite delignification procedure described in Section 5.2.2.2 except that the blocks were not numbered prior to delignification. The total combined dry weight of the twenty five blocks was measured prior to delignification and after each chlorite/water treatment. The percentage weight losses of the blocks after four acid chlorite/water treatments were 20.02% and 25.24% for lime and pine blocks respectively. After delignification was completed, the blocks were numbered, oven-dried at 102°C for 3 hours and weighed individually.

The periodate blocks of lime and pine were prepared following the procedure described in Section 5.2.3.2. The thirty blocks of each wood species were split into two groups of fifteen which were treated separately. A total dry weight was obtained for each set of fifteen blocks prior to acetone/water extraction and again after periodate treatment. The percentage weight losses of the blocks after six periodate/water treatments were 79.71% and 74.07% for lime and pine respectively. The periodate blocks were small and too brittle to be marked with a number and they were therefore separated into groups of five which were stored in separate glass petri dishes.

The blocks were oven-dried at 102°C for 3 hours and a combined dry-weight was obtained for each set of five blocks.

5.2.6.2 Preparation of CCA solution

A 3% $\frac{w}{v}$ CCA solution (type C) was prepared according to BS4072 (1974) (Chapter 2, Section 2.2.2).

5.2.6.3 Impregnation and curing of blocks

All blocks were impregnated with 3% $\frac{w}{v}$ CCA solution using the method described for CCA and ACA treated blocks in Chapter 3 (Section 3.2.1.4). The blocks were soaked in the preservative solution for 30 minutes.

The treated blocks were cured wet for 2 weeks in sealed glass petri dishes containing moistened tissue paper and were turned once every 2 days by inverting the petri dish. After 2 weeks, the tissue paper was removed and during the third week of curing, the lid of the petri dish was gradually opened. At the end of the third week, the lid was removed and the blocks were allowed to air-dry in the open petri dish for a further week.

Five CCA treated blocks of each wood type were set aside as unleached control blocks. All remaining blocks were subjected to an aqueous leaching programme.

5.2.6.4 Aqueous leaching of blocks

Blocks were leached in groups of five in 200 cm^3 distilled water at room temperature for 6 days with daily changes of water (Chapter 3, Section 3.2.2.1). The individual daily leachates were stored separately for chemical analysis.

5.2.6.5 Chemical analysis of blocks and leachates

All leached blocks and unleached controls were digested in concentrated H_2SO_4 and "100 volume" H_2O_2 and analysed for copper, chromium and arsenic contents using a standard additions technique on an A.A.S. (Chapter 3, Section 3.2.2.1). The periodate blocks were too small for individual analysis. Therefore each set of five periodate blocks was digested and analysed as a single sample with $\% \frac{w}{w}$ copper, chromium and arsenic content expressed as a percentage of the combined dry weight of the blocks prior to CCA treatment.

The daily leachates were acidified, filtered, diluted and analysed individually for copper, chromium and arsenic contents by a standard additions method on an A.A.S. (Chapter 3, Section 3.2.2.1).

The concentration of arsenic in the leachates was too low to be detected by the A.A.S. Therefore, amounts of arsenic lost from blocks during leaching could only be

determined by comparison of mean analytical arsenic concentrations of leached and unleached blocks and percentage loss of arsenic from blocks during leaching was calculated using these values. Percentage loss calculated in this way is subject to error caused by variations in both uptake of preservative solution and selective absorption of preservative elements between blocks during impregnation.

Percentage losses of copper and chromium from blocks during leaching were calculated using the analytical concentrations in leachates and in leached blocks (see Chapter 3, Section 3.2.2.1) and were therefore not subject to the errors described above.

5.3 Results

5.3.1 Studies on lignin nitrogen and copper in untreated and ACA treated pine during soil burial

5.3.1.1 Weight loss and % $\frac{W}{W}$ nitrogen data

Mean percentage weight losses (± standard deviations) for untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial are presented in Table 5.5. The mean values are also presented graphically in Fig 5.3. Untreated blocks showed continued weight loss throughout the burial period, reaching nearly 22% weight loss by the 18 week sampling interval. The ACA treated blocks only showed weight losses beyond the 12 week sampling interval and only showed 5% loss in weight by the end of the burial period. The weight loss values for both the untreated and ACA treated blocks are very similar to those found for the identically treated pine blocks analysed as part of the main ACA burial study (Chapter 4, Fig 4.2).

Mean % $\frac{W}{W}$ nitrogen content (± standard deviations) for the untreated and ACA treated pine blocks during soil burial are presented in Table 5.6. These values are derived from the analysis of blocks from the main ACA burial study. The mean values are also presented graphically in Fig 5.4. The nitrogen content of untreated blocks rose continuously throughout the burial period, reaching 0.376% $\frac{W}{W}$ nitrogen by the 18 week sampling interval.

The nitrogen contents of the ACA treated blocks fell during the first 6 weeks of soil burial but subsequently rose again between 6 and 12 weeks, with no further increase in nitrogen content beyond 12 weeks.

5.3.1.2. Periodate lignin content

It should be noted that the periodate lignin isolation procedure used in this study is an oxidative process which may cause some solubilisation of lignin. Therefore, the periodate procedure does not give a quantitative yield of wood lignin and the lignin yield might be particularly low in decayed wood samples. Consequently, calculated values for percentage lignin, mg of lignin nitrogen per g of wood, mg of lignin copper per g of wood and percentages of total wood nitrogen and copper bound to lignin are underestimates of the true values and cannot be considered accurate determinations.

The periodate lignin contents of the untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial, expressed as a percentage of the pre-burial dry mass of blocks, are presented in Table 5.7 and graphically in Fig 5.5. The percentage periodate lignin content of untreated blocks decreased continuously during soil burial whereas the lignin content of the ACA treated blocks only decreased beyond the 12 week sampling interval when decay also commenced.

The periodate lignin contents, expressed as a percentage of the extractive-free dry mass of wood after burial, are presented in Table 5.8 Percentage lignin contents, expressed in this way, remained constant through the burial period, despite considerable decay in the case of untreated blocks.

5.3.1.3. Lignin nitrogen contents

The mean % $\frac{w}{w}$ nitrogen contents ($\pm$ standard deviations) of the periodate lignin fractions of untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks during soil burial are presented with the values for whole blocks in Table 5.6. In untreated blocks, nitrogen accumulated on the lignin throughout the burial period, the nitrogen content of the lignin increased from 0.104% $\frac{w}{w}$ for unburied controls to 0.733% $\frac{w}{w}$ for blocks exhumed at the 18 week sampling interval. The nitrogen content of the lignin fraction of ACA treated blocks only increased beyond the 6 week sampling interval, showing a considerable increase from 0.302% $\frac{w}{w}$ to 0.535% $\frac{w}{w}$ between 12 and 18 weeks.

In Table 5.9, the % $\frac{w}{w}$ nitrogen contents of the lignin fractions have been converted to milligrams of nitrogen per gram of periodate lignin. These latter values are simply a factor of ten times greater than the % $\frac{w}{w}$ nitrogen contents (Section 5.2.5.3) and therefore show the same trends.

The milligrams of lignin nitrogen per gram of wood for untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks during soil burial are presented in Table 5.10 and graphically in Fig 5.6. These values were calculated using the percentage periodate lignin contents based on the pre-burial dry masses of the blocks (see Section 5.2.5.3) and therefore take account of the depletion of lignin during the decay process. In untreated wood, the amount of lignin-bound nitrogen increased continuously throughout the burial period from 0.282 to 1.569 mg of lignin nitrogen per g of wood (more than a fivefold increase). Total wood nitrogen content (Fig 5.4) and percentage weight loss (Fig 5.3) of untreated blocks also increased continuously throughout soil burial.

Comparison of values for untreated and ACA treated unburied control blocks show, as expected, that the ACA treated blocks contained considerably more lignin-bound nitrogen (0.623 mg of nitrogen per g of ACA treated wood compared to 0.282 mg of nitrogen per g of untreated wood). However, during soil burial, the ACA treated blocks showed less accumulation of lignin-bound nitrogen than the untreated blocks and after 18 weeks of soil burial contained 1.311 mg of lignin-bound nitrogen per g compared with 1.57 mg of lignin nitrogen per g of untreated wood. Accumulation of lignin

nitrogen in the ACA treated blocks only commenced after the 6 week sampling interval when the first increase in total wood nitrogen content was also observed (Fig 5.4) and the majority of the build up in lignin nitrogen in ACA treated blocks was between 12 and 18 weeks of soil burial, corresponding to the onset of decay (Fig 5.3). During this latter period, the rate of accumulation of lignin nitrogen in ACA treated blocks was similar to that observed in untreated blocks (Fig 5.6).

5.3.1.4 Percentage of total wood nitrogen on lignin

Data for lignin nitrogen expressed as a percentage of total wood nitrogen for both untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks are presented in Table 5.11 and graphically in Fig 5.7. Both untreated and ACA treated blocks showed an increase in the percentage of total nitrogen bound to lignin during soil burial. Untreated blocks showed a gradual increase in the percentage of total nitrogen on lignin beyond the 6 week sampling interval from about 35% to 41.72%. The ACA treated blocks showed an initial increase in percentage nitrogen on lignin from 20.76% to 31.65% during the first 6 weeks of soil burial. This change

coincided with a fall in total wood nitrogen content from 0.300 to 0.201% $\frac{w}{w}$. The percentage of total nitrogen on lignin then increased considerably beyond the 12 week sampling interval from 29.65% to 49.65%. Therefore, after 18 weeks of soil burial, the ACA treated blocks had a larger percentage of total nitrogen on lignin than the untreated blocks, although both the total nitrogen and lignin nitrogen contents were higher for the untreated blocks.

5.3.1.5 Copper data

Mean copper contents ($\pm$ standard deviations) of the lignin fraction and whole blocks of untreated and 0.071% $\frac{w}{v}$ ACA treated pine are presented in Table 5.12. The values for the whole blocks are derived from the analysis of blocks from the main ACA burial study. The periodate lignin fractions isolated from both untreated and ACA treated blocks invariably contained less copper on a % $\frac{w}{w}$ basis than the whole blocks. The copper contents of the lignin of ACA treated blocks were below 0.020% $\frac{w}{w}$ and therefore only marginally exceeded the background levels found in whole untreated blocks.

Table 5.13 shows the milligrams of copper per gram of periodate lignin for the untreated and ACA treated

pine blocks. These values are simply a factor of ten times greater than the % $\frac{w}{w}$ copper values for periodate lignin fractions.

The milligrams of lignin bound copper per gram of wood for both untreated and ACA treated blocks are presented in Table 5.14. These values are based on the pre-burial dry mass of blocks and therefore take account of the depletion of lignin during decay. However, neither untreated nor ACA treated blocks showed a significant change in the amount of lignin-bound copper during soil burial and the values for the treated blocks were only approximately double those of the untreated blocks.

Data for lignin copper expressed as a percentage of total wood copper for untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks are presented in Table 5.15. For untreated blocks, less than 20% of the toal wood copper was generally found on the lignin, although the periodate lignin fraction constituted over 27% of the total wood substance prior to decay. For the ACA treated blocks, (which contained more copper than the untreated blocks

on a % $\frac{w}{w}$ basis) only a very small proportion (less than 7%) of the copper was found on the periodate lignin fraction.

5.3.2 Leaching studies on CCA treated periodate lignin, holocellulose and normal wood

The mean analytical % $\frac{w}{w}$ copper, chromium and arsenic contents($\pm$standard deviations) of leached and unleached CCA treated normal, delignified and periodate lime and pine blocks are presented in Table 5.16. The values for unleached periodate lignin represent the analysis of 5 blocks grouped together and therefore have no standard deviation. With the exception of chromium values for normal and delignified lime blocks, analytical concentrations of all preservative elements were lower in leached blocks than in the unleached controls. For both lime and pine, the concentrations (on a % $\frac{w}{w}$ basis) of all three preservative elements were highest in delignified blocks and lowest in periodate blocks. This pattern was observed both before and after aqueous leaching of blocks.

5.3.2.1 Selective absorption ratios

Selective absorption ratios for each preservative element were calculated for each individual wood block using

the analytical preservative data and preservative contents derived from uptake of CCA soltuion by blocks (see Chapter 2, Section 2.3.3). The mean ratios (± standard deviations) of each preservative element for each wood type are presented in Table 5.17. With the exception of the data for copper in normal and delignified lime blocks, all selective absorption ratios for all elements exceeded one. The ratio for each wood type was invariably highest for arsenic and lowest for copper. However, there were no clear differences in the ratio of each element between different wood types. The ratios for chromium and arsenic were lowest in delignified blocks of both lime and pine. However, the ratios of chromium and arsenic were highest in periodate lignin blocks of lime and normal wood blocks of pine. The differences in the ratio of copper between wood types were less distinct.

5.3.2.2 Percentage loss of preservative elements

Percentage losses of copper, chromium and arsenic from CCA treated normal, delignified and periodate lime and pine blocks during aqueous leaching are presented in Table 5.18. Copper and chromium losses were calculated using the analytical preservative contents of leachates and leached blocks whereas arsenic losses were calculated from mean analytical preservative contents of blocks before and after leaching.

For both lime and pine, percentage losses of copper during leaching were greatest in delignified wood (22.54 and 30.53% for delignified lime and pine blocks respectively) and lowest in normal wood (10.02 and 10.63% for normal lime and pine blocks respectively). Periodate lignin blocks of both lime and pine lost about 18% of their copper.

Percentage losses of chromium were far lower than percentage copper losses for all wood types. However, chromium losses were also greatest from delignified wood (4.75 and 8.10% from delignified lime and pine blocks respectively). Losses of chromium from normal and periodate blocks of both wood species were minimal (less than 2.5%).

Percentage losses of arsenic, being calculated from the analytical data of leached and unleached blocks alone are not as reliable as the percentage loss data for copper and chromium (see Section 5.2.6.5). However, percentage losses of arsenic were apparently similar from normal and delignified blocks for both lime and pine (13.38 and 16.71% respectively for normal and delignified lime blocks and 9.82 and 7.79% respectively for normal and delignified pine blocks). Periodate blocks of both wood species showed the lowest percentage losses of arsenic (5.91 and 1.82% for periodate lime and pine respectively).

5.3.2.3 Atom ratios for preservative elements

The atom ratios of copper, chromium and arsenic in CCA treated normal, delignified and periodate lime and pine blocks before and after aqueous leaching were calculated from the analytical preservative data (Table 5.16). The atom ratios of copper : chromium : arsenic are presented in Table 5.19.

The ratio for the 3% $\frac{W}{V}$ CCA treating solution was 1 : 2.183 : 1.057 (Cu : Cr : As). In unleached blocks of all wood types, the ratios of both chromium and arsenic relative to copper were higher than in the treating solution. Delignified lime and pine blocks showed the smallest increase in the ratio of chromium relative to copper during CCA treatment; the ratio increased from 2.183 : 1 in the treating solution to 2.263 and 2.382 : 1 in unleached delignified lime and pine respectively. Normal and periodate lime and pine blocks showed larger increases in the ratio of chromium to copper during CCA treatment (the ratio of chromium to copper was at least 2.6 : 1 in all except the normal lime blocks).

The atom ratio for arsenic relative to copper rose from 1.057 : 1 in the treating solution to 1.381 and 1.273 : 1 in unleached delignified blocks of lime and pine respectively. Normal and periodate lime and pine blocks also showed larger increases in the ratio of arsenic to

copper during CCA treatment than the delignified blocks; the ratio of arsenic to copper exceeded 1.4: 1 in all cases except normal pine blocks.

Aqueous leaching of blocks of all wood types led to a further increase in the ratio of chromium and arsenic relative to copper. There were large increases in the ratio of chromium to copper in leached delignified and periodate blocks of both lime and pine (the ratio approached or exceeded 3:1) whereas there was only a much smaller increase in the ratio of chromium to copper in leached normal lime and pine blocks (the ratio remained below 2.8 : 1).

Increases in the ratio of arsenic relative to copper during aqueous leaching were generally much smaller than the increases in the chromium ratio.

FIG 5.3

MEAN % WEIGHT LOSS OF UNTREATED AND ACA TREATED PINE BLOCKS DURING SOIL BURIAL

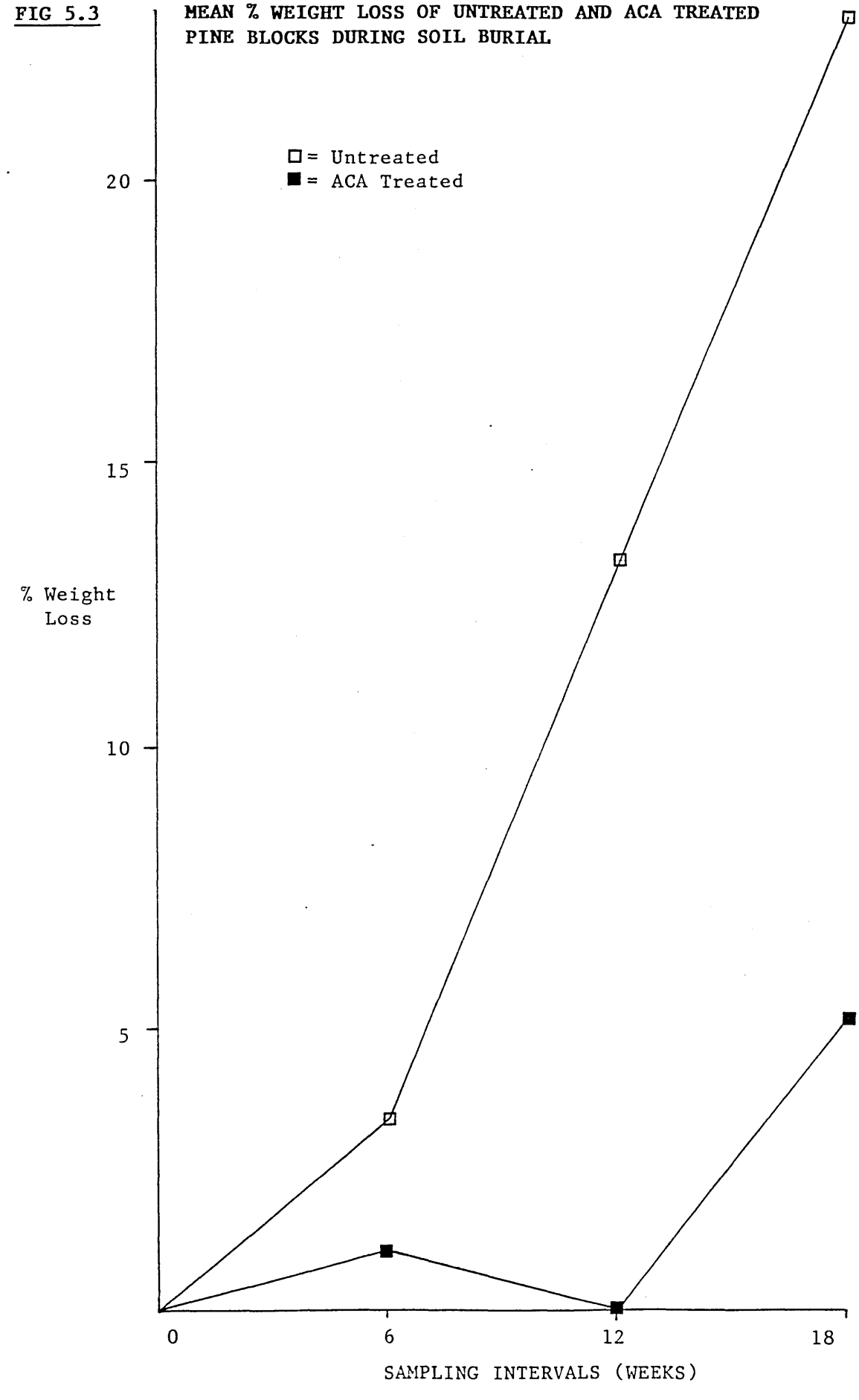


FIG 5.4 MEAN $\%^{w}_{w}$ NITROGEN CONTENTS OF UNTREATED AND ACA TREATED PINE BLOCKS DURING SOIL BURIAL

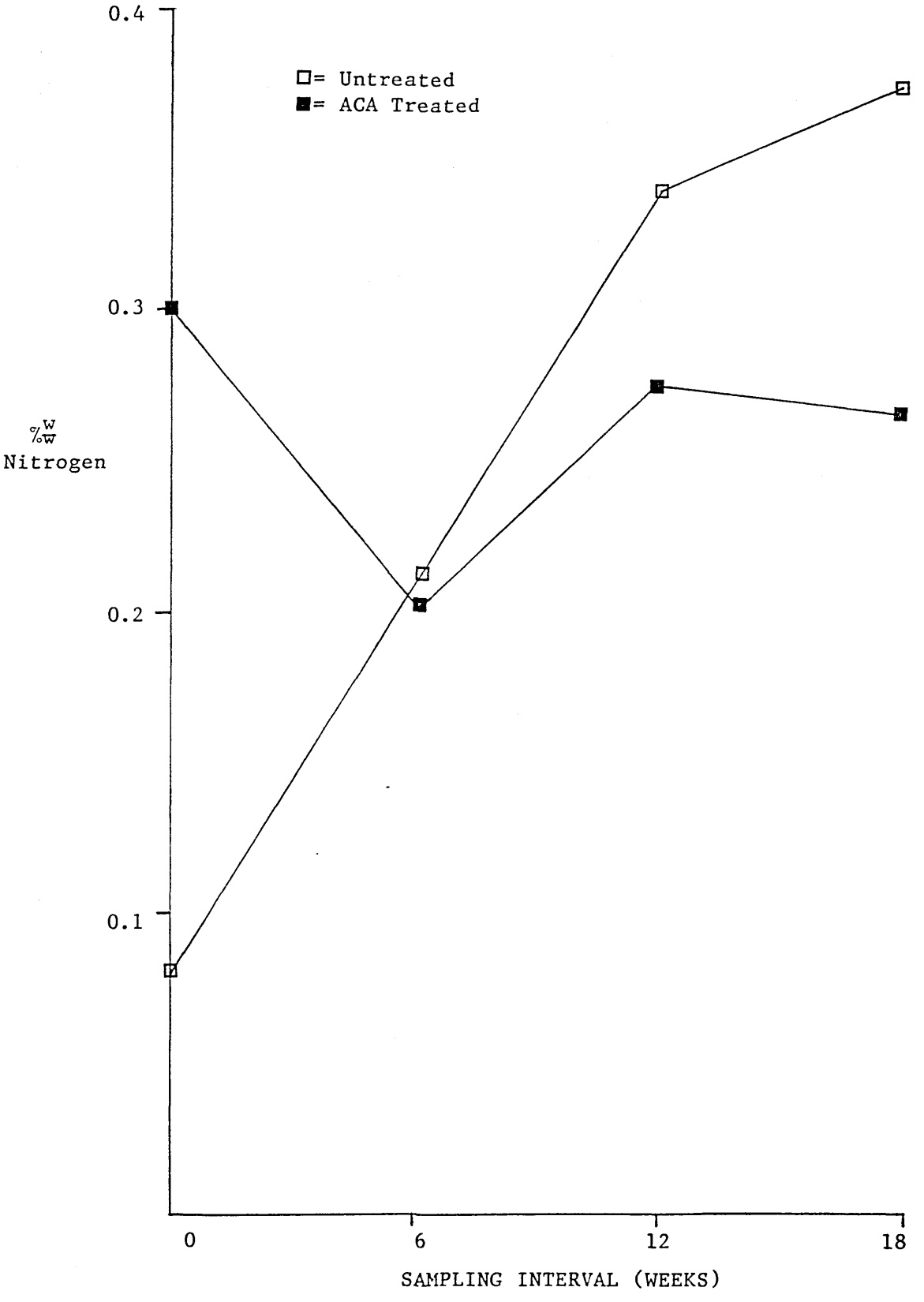


FIG 5.5 PERCENTAGE LIGNIN CONTENT OF UNTREATED AND ACA TREATED PINE BLOCKS DURING SOIL BURIAL

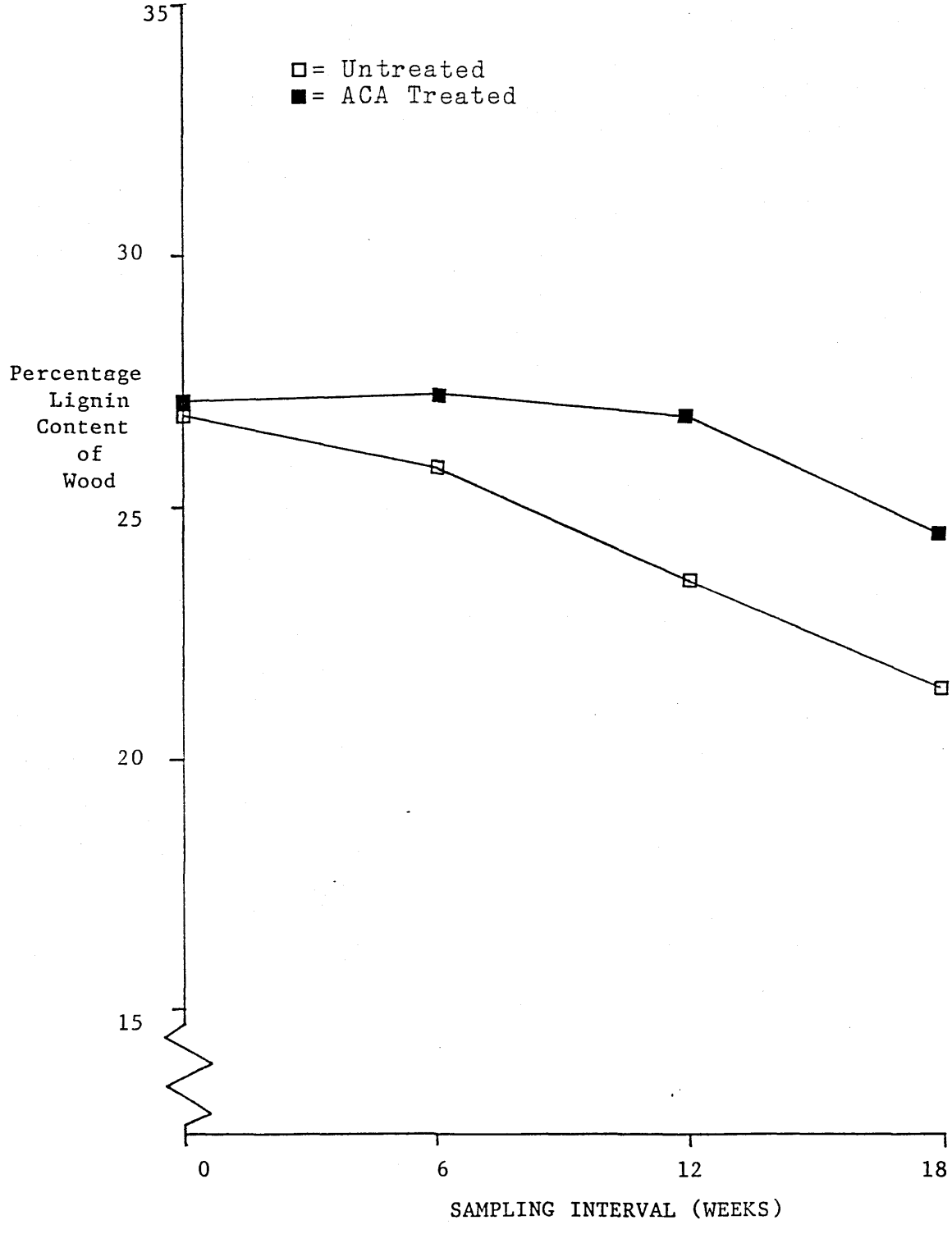


FIG 5.6 MILLIGRAMS OF LIGNIN NITROGEN PER GRAM OF WOOD FOR UNTREATED AND ACA TREATED PINE BLOCKS DURING SOIL BURIAL

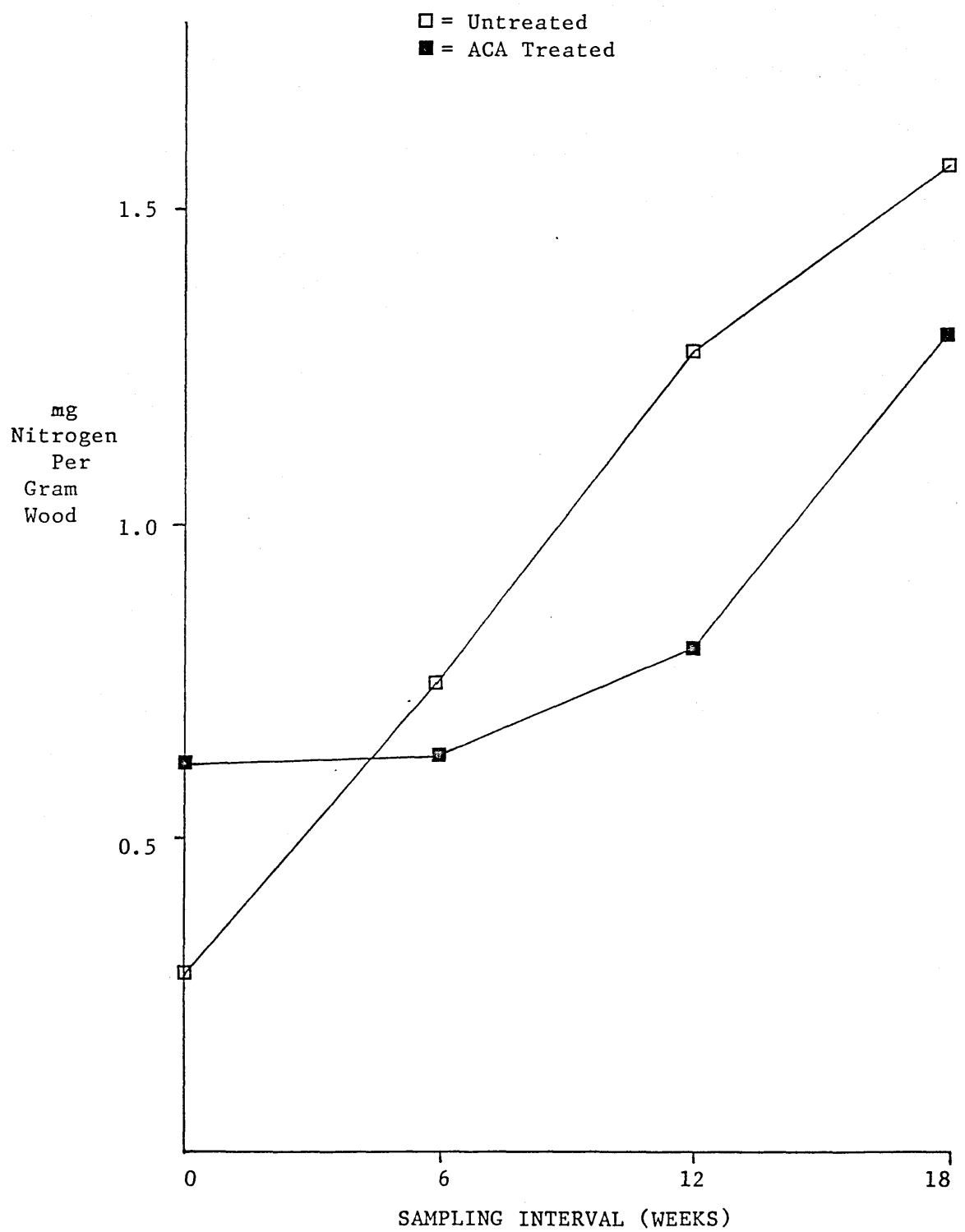


FIG 5.7 PERCENTAGE OF TOTAL NITROGEN ON LIGNIN FOR UNTREATED AND ACA TREATED PINE BLOCKS DURING SOIL BURIAL

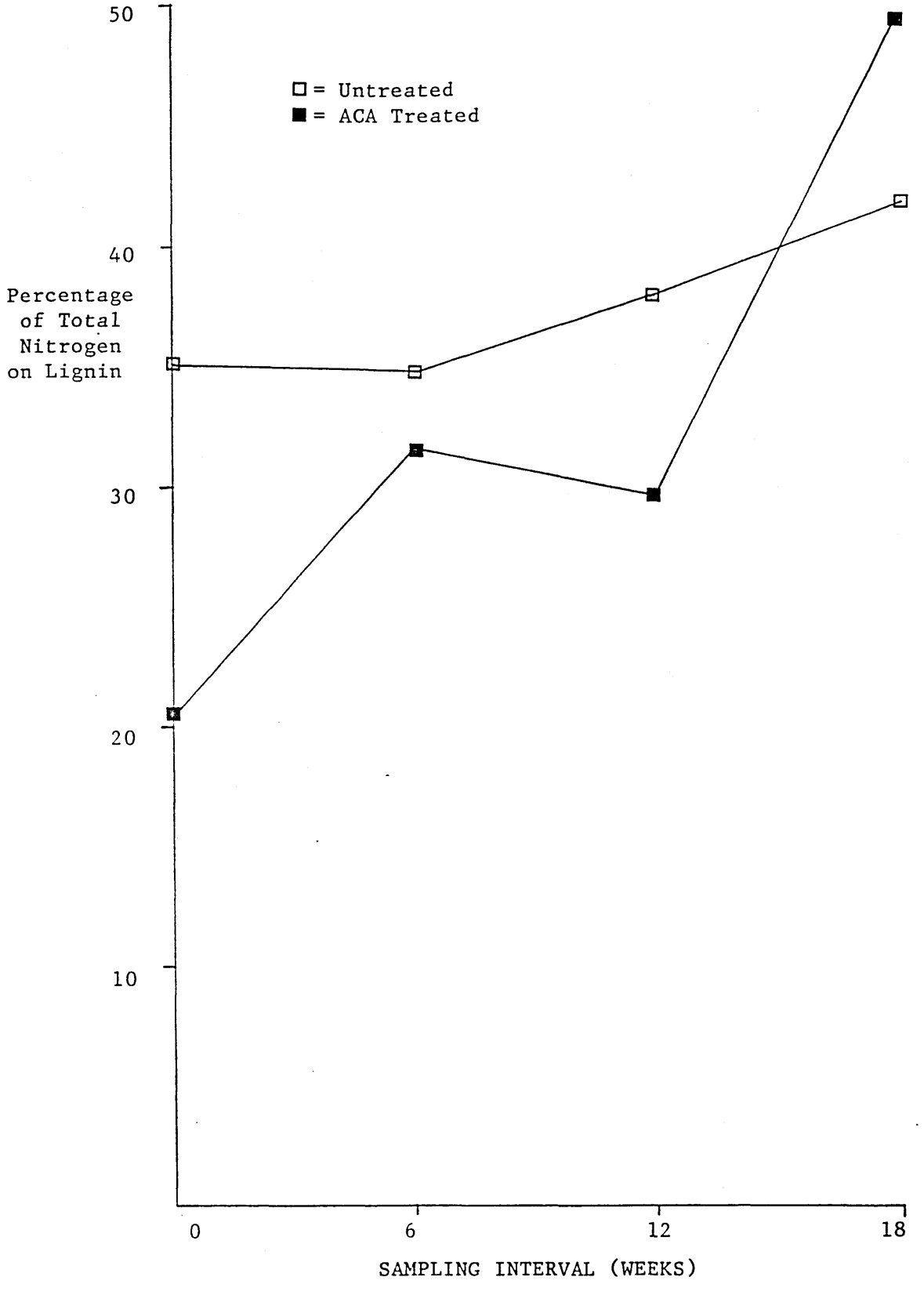


Table 5.5

Mean % weight losses (± standard deviations) for untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial

Treatment	Percentage weight loss		
	Sampling interval (weeks)		
	6	12	18
Untreated Pine	3.04 ± 1.01	13.81 ± 1.39	21.69 ± 1.18
0.071% $\frac{W}{V}$ ACA Treated Pine	1.07 ± 0.81	0.83 ± 0.81	5.32 ± 2.40

The "+" above the value for ACA treated pine at 12 weeks denotes a weight gain.

Table 5.6

Mean % $\frac{W}{W}$ nitrogen contents (± standard deviations) for untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial, determined on the whole blocks and on the periodate lignin fractions

Treatment	Fraction analysed	% $\frac{W}{W}$ Nitrogen concentration			
		Sampling Interval (weeks)			
		0	6	12	18
Untreated Pine	Whole Wood	0.080 ±0.005	0.215 ±0.012	0.340 ±0.024	0.376 ±0.007
Untreated Pine	Periodate Lignin	0.104 ±0.003	0.289 ±0.006	0.547 ±0.022	0.733 ±0.028
0.071% $\frac{W}{V}$ ACA Treated Pine	Whole Wood	0.300 ±0.030	0.201 ±0.017	0.274 ±0.016	0.264 ±0.019
0.071% $\frac{W}{V}$ ACA Treated Pine	Periodate Lignin	0.229 ±0.017	0.233 ±0.007	0.302 ±0.013	0.535 ±0.033

Table 5.7

Percentage periodate lignin contents of untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks during soil burial, expressed as a percentage of the pre-burial dry mass of blocks

Treatment	Percentage Periodate Lignin			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	27.1	25.9	23.6	21.4
0.071% $\frac{w}{v}$ ACA Treated Pine	27.2	27.3	26.9	24.5

Table 5.8

Percentage periodate lignin contents of untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks during soil burial, expressed as a percentage of the extractive-free dry mass of exhumed blocks

Treatment	Percentage Periodate Lignin			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	28.3	27.9	28.6	28.2
0.071% $\frac{w}{v}$ ACA Treated Pine	28.4	27.6	28.0	26.9

Table 5.9

Milligrams of nitrogen per gram of periodate lignin for untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial

Treatment	mg Nitrogen/g Periodate Lignin			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	1.04	2.89	5.47	7.33
0.071% $\frac{W}{V}$ ACA Treated Pine	2.29	2.33	3.02	5.35

Table 5.10

Milligrams of lignin nitrogen per gram of wood for untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial, based on the pre-burial dry masses of blocks

Treatment	mg Lignin Nitrogen/g Wood			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	0.282	0.749	1.291	1.569
0.071% $\frac{W}{V}$ ACA Treated Pine	0.623	0.636	0.812	1.311

Table 5.11

Percentage of total wood nitrogen present in the periodate lignin fraction of untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial

Treatment	Percentage of Wood Nitrogen in Lignin			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	35.23	34.81	37.97	41.72
0.071% $\frac{W}{V}$ ACA Treated Pine	20.76	31.65	29.65	49.65

Table 5.12

Mean % $\frac{W}{W}$ copper contents (± standard deviations) for untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial, determined on the whole blocks and on the periodate lignin fractions

Treatment	Fraction Analysed	% $\frac{W}{W}$ Copper Concentration			
		Sampling Interval (weeks)			
		0	6	12	18
Untreated Pine	Whole Blocks	0.009 ±0.002	0.016 ±0.003	0.014 ±0.002	0.014 ±0.001
Untreated Pine	Periodate Lignin	0.007 ±0	0.009 ±0.011	0.011 ±0.002	0.011 ±0.001
0.071% $\frac{W}{V}$ ACA Treated Pine	Whole Blocks	0.098 ±0.007	0.075 ±0.007	0.075 ±0.004	0.070 ±0.008
0.071% $\frac{W}{V}$ ACA Treated Pine	Periodate Lignin	0.016 ±0.001	0.017 ±0.001	0.017 ±0.001	0.018 ±0.001

Table 5.13

Milligrams of copper per gram of periodate lignin for untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks during soil burial

Treatment	mg Copper/g Periodate Lignin			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	0.07	0.09	0.11	0.11
0.071% $\frac{w}{v}$ ACA Treated Pine	0.16	0.17	0.17	0.18

Table 5.14

Milligrams of lignin copper per gram of wood for untreated and 0.071% $\frac{w}{v}$ ACA treated pine blocks during soil burial, based on the pre-burial dry masses of blocks

Treatment	mg Lignin Copper/g Wood			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	0.019	0.023	0.026	0.024
0.071% $\frac{w}{v}$ ACA Treated Pine	0.044	0.046	0.046	0.044

Table 5.15

Percentage of total wood copper present in the periodate lignin fraction of untreated and 0.071% $\frac{W}{V}$ ACA treated pine blocks during soil burial

Treatment	Percentage of Wood Copper in Lignin			
	Sampling Interval (weeks)			
	0	6	12	18
Untreated Pine	21.08	14.57	18.54	16.81
0.071% $\frac{W}{V}$ ACA Treated Pine	4.44	6.19	6.10	6.29

Table 5.16

Mean analytical % $\frac{w}{w}$ copper, chromium and arsenic contents (± standard deviations) of leached and unleached CCA treated normal, delignified and periodate lime and pine blocks

Wood Type	Concentration by Analysis (% $\frac{w}{w}$)					
	Copper		Chromium		Arsenic	
	Un-Leached	Leached	Un-Leached	Leached	Un-Leached	Leached
Normal Lime	0.364 ±0.038	0.334 ±0.026	0.709 ±0.054	0.710 ±0.068	0.680 ±0.044	0.589 ±0.049
Delignified Lime	0.507 ±0.036	0.405 ±0.014	0.940 ±0.122	0.943 ±0.070	0.826 ±0.063	0.688 ±0.064
Periodate Lime	0.262	0.221 ±0.008	0.571	0.560 ±0.010	0.491	0.462 ±0.013
Normal Pine	0.456 ±0.033	0.358 ±0.029	0.972 ±0.051	0.804 ±0.076	0.713 ±0.016	0.643 ±0.045
Delignified Pine	0.633 ±0.017	0.472 ±0.019	1.235 ±0.081	1.114 ±0.072	0.950 ±0.069	0.876 ±0.061
Periodate Pine	0.321	0.271 ±0.009	0.683	0.677 ±0.024	0.548	0.538 ±0.013

Table 5.17

Selective absorption ratios (± standard deviations) for copper, chromium and arsenic in 3% $\frac{w}{v}$ CCA treated normal, delignified and periodate lime and pine blocks

Wood Type	Selective Absorption Ratios		
	Copper	Chromium	Arsenic
Normal Lime	0.980 ±0.035	1.070 ±0.061	1.472 ±0.054
Delignified Lime	0.992 ±0.058	1.026 ±0.081	1.300 ±0.130
Periodate Lime	1.008	1.231	1.515
Normal Pine	1.172 ±0.129	1.398 ±0.121	1.468 ±0.045
Delignified Pine	1.054 ±0.022	1.149 ±0.053	1.269 ±0.090
Periodate Pine	1.013	1.207	1.387

Table 5.18

Mean percentage loss (± standard deviations) of copper, chromium and arsenic from CCA treated normal, delignified and periodate lime and pine blocks during aqueous leaching

Wood Type	Percentage Loss of Preservative Elements during Leaching		
	Copper	Chromium	Arsenic
Normal Lime	10.02 ± 0.26	1.68 ± 0.19	13.38
Delignified Lime	22.54 ± 1.47	4.75 ± 0.19	16.71
Periodate Lime	18.29 ± 1.48	1.22 ± 0.35	5.91
Normal Pine	10.63 ± 0.64	1.50 ± 0.12	9.82
Delignified Pine	30.53 ± 2.14	8.10 ± 0.65	7.79
Periodate Pine	17.84 ± 1.03	2.19 ± 0.28	1.82

Percentage losses of copper and chromium were calculated from the analytical preservative contents of leachates and leached blocks.

Percentage losses of arsenic were calculated from the mean arsenic contents of leached and unleached blocks.

Table 5.19

Atom ratios of copper, chromium and arsenic in CCA treated normal, delignified and periodate lime and pine blocks before and after aqueous leaching

Wood Type	Atom Ratio (Cu:Cr:As)	
	Unleached Blocks	Leached Blocks
Normal Lime	1:2.378:1.583	1:2.598:1.495
Delignified Lime	1:2.263:1.381	1:2.849:1.442
Periodate Lime	1:2.663:1.589	1:3.104:1.778
Normal Pine	1:2.607:1.327	1:2.741:1.522
Delignified Pine	1:2.382:1.273	1:2.885:1.576
Periodate Pine	1:2.600:1.448	1:3.051:1.683

The atom ratio for copper : chromium : arsenic in the 3% $\frac{w}{v}$ CCA treating solution was:

1 : 2.183 : 1.057

5.4 Discussion

5.4.1 Studies on lignin nitrogen and copper in untreated and ACA treated pine during soil burial

In terms of the aims of this experiment, the following major conclusions can be drawn:

1. Prior to burial in soil, both untreated and ACA treated blocks contained some lignin-bound nitrogen (Table 5.10) and ACA treated wood contained more lignin nitrogen than untreated wood. However, a smaller percentage of total wood nitrogen was bound to lignin in ACA treated blocks than in untreated blocks (Table 5.11).

2. In both untreated and ACA treated wood, nitrogen accumulated on lignin during soil burial (Table 5.10, Fig 5.6). This accumulation of nitrogen on lignin was generally associated with a corresponding increase in the total nitrogen content of the wood (Fig 5.4) and with decay, as measured by percentage weight loss (Fig 5.3). In untreated blocks, nitrogen accumulation on lignin occurred throughout the whole burial period, whilst ACA treated blocks showed no such accumulation until after the 6 week sampling interval (Fig 5.6). The ACA treated blocks accumulated less lignin-bound nitrogen than untreated blocks during soil burial. However, once decay of the ACA treated blocks commenced (beyond 12 weeks), the rate of lignin-nitrogen accumulation by these blocks was similar to the rate observed in untreated blocks (Fig 5.6).

3. The percentage of total nitrogen bound to lignin increased during soil burial for both untreated and ACA treated blocks (Table 5.11, Fig 5.7) and after 18 weeks of soil burial, ACA treated blocks contained a higher percentage of lignin nitrogen than untreated blocks, despite having lower total nitrogen and lignin nitrogen contents.

4. Only a small amount of copper (less than 0.05 mg per g of wood) was isolated with the periodate lignin fraction of unburied ACA treated wood (Table 5.14), amounting to less than 5% of the total wood copper (Table 5.15). Such a low lignin copper content for ACA treated wood was most probably caused by removal of copper from lignin during periodate treatment. Changes, during soil burial, in both the amount of copper isolated on lignin (Table 5.14) and the percentage of total wood copper isolated on lignin (Table 5.15) were small and followed no obvious pattern.

Untreated pine blocks showed continued decay, as determined by weight loss, throughout the burial period (Fig 5.3). This decay was also accompanied by a continuous increase in the $\% \frac{w}{w}$ nitrogen content of the blocks over the same period (Fig 5.4), again confirming that nitrogen accumulation, resulting from microbial invasion of the wood, is an integral part of the decay process in soil.

The 0.071% $\frac{w}{v}$ ACA treated pine blocks only showed decay beyond the 12 week sampling interval (Fig 5.3). These

blocks had a higher % $\frac{w}{w}$ nitrogen content than untreated blocks prior to soil burial due to ACA treatment and showed a fall in nitrogen content during the first 6 weeks of soil burial (Fig 5.4) corresponding with a loss of soluble nitrogenous compounds from the wood (Chapter 4). The nitrogen content then increased again between 6 and 12 weeks, prior to the onset of decay. The slight fall in the nitrogen content of these blocks beyond 12 weeks may be an anomaly, since nitrogen accumulation in the blocks would be expected to continue as they decayed.

The periodate lignin contents of untreated blocks, expressed as a percentage of their pre-burial dry mass (Table 5.7, Fig 5.5) decreased throughout the burial period as decay continued. ACA treated blocks only showed a fall in percentage periodate lignin content, expressed in this way, beyond the 12 week sampling interval, when decay was first observed. Therefore lignin was apparently depleted from the untreated and ACA treated blocks during the decay process. Periodate lignin contents of both untreated and ACA treated blocks, expressed as a percentage of post-burial extractive-free dry weight (Table 5.8), remained constant throughout the burial period, showing that the lignin was depleted from the blocks at a rate similar to the depletion rate of the rest of the wood constituents.

The observed depletion of lignin may be as a result of degradation by micro-organisms. The soft-rot fungus **Chaetomium globosum** has been shown to cause a gradual depletion of lignin from wood (Levi and Preston, 1965) but soft-rot attack alone would be unlikely to deplete lignin at the rate observed in this experiment. The presence of white-rotting basidiomycetes might account for rapid degradation of the lignin but such fungi decaying ACA treated wood would have to be tolerant to both copper and arsenic. The high nitrogen content of the ACA treated wood might facilitate this. Alternatively, if the lignin remained undecayed during soil burial, the degradation and removal of the polysaccharides by micro-organisms may have rendered the lignin susceptible to excessive oxidation during the latter stages of periodate treatment, resulting in some solubilisation of lignin in decayed wood samples. If such solubilisation of wood lignin did occur during periodate treatment of decayed blocks, the calculated values for percentage periodate lignin (table 5.7, Fig 5.5), mg of lignin nitrogen per g of wood (Table 5.10, Fig 5.6) mg of lignin copper per g of wood (table 5.14) and hence percentage of total wood nitrogen and copper associated with lignin (tables 5.11 and 5.15) would be underestimates of the actual values. However, Wald, Ritchie and Purves (1949), using periodate

lignin isolated from undecayed wood, found only a 15% weight loss in such periodate lignin subjected to six further treatments with periodate solution beyond the six cycles required to remove all polysaccharides. Therefore, in the present experiment, unless the lignin was considerably modified during the burial of blocks in soil, it is unlikely that much lignin was lost as a result of excessive oxidation by periodate and inaccuracies in calculated values are thus probably small.

Since the periodate lignin contents of wood blocks fell during soil burial, changes in the lignin nitrogen contents of the total blocks could only be monitored using data for mg of lignin nitrogen per gram of wood (table 5.10, Fig. 5.6) and percentage of total wood nitrogen associated with lignin (table 5.11, Fig. 5.7), since these values were calculated using the pre-burial dry masses of blocks. (*See section 5.3.1.2)

Untreated pine blocks not subjected to soil burial contained 0.282 mg of lignin nitrogen per gram of wood (Table 5.10), amounting to 35% of the total wood nitrogen (Table 5.11). Therefore, even prior to soil burial

untreated pine contained some lignin-bound nitrogen. Such lignin nitrogen may have originated from aromatic nitrogenous compounds, produced as intermediates in the shikimic acid pathway, which may become incorporated into lignin with the oxyphenylpropane units. Alternatively, ammonium ions and amino acids present in living wood cells may become chemically combined to lignin during lifnigication of the cells.

Comparison of untreated and ACA treated blocks for total nitrogen and lignin nitrogen content prior to soil burial (Tables 5.6 and 5.10) shows that the ACA treated blocks not only contained more nitrogen in the whole wood than untreated blocks but also contained more lignin-bound nitrogen (0.623 mg per g of ACA treated wood compared to 0.282 mg per g of untreated wood). Therefore, some of the extra nitrogen added to wood during ACA treatment, probably in the form of ammonium or cuprammonium ions, clearly becomes bound to lignin. Both of these ions could bind to lignin by either cation exchange or complexing mechanisms.

Ammonium nitrogen analysis of ACA treated wood blocks using concentrated NaOH (Chapter 3) would be expected to recover all soluble ammonium compounds, ammonia complexed to preservative elements and ammonium ions fixed to the wood by cation exchange mechanisms. However,

not all of the extra nitrogen present in the wood as a result of ACA treatment could be recovered as ammonium nitrogen, suggesting that some of the ammonia from the ACA treating solution becomes permanently bound to wood constituents, possibly by covalent bonding to functional groups such as phenolic groups on lignin as a result of condensation reactions.

Although the lignin nitrogen content was higher in ACA treated blocks than in untreated blocks, prior to soil burial, the percentage of total wood nitrogen bound to lignin was much lower in the treated blocks (Table 5.11). During ACA treatment, the total nitrogen content of the wood was increased from 0.080% $\frac{w}{w}$ to 0.300 % $\frac{w}{w}$ (Table 5.6), representing an increase of 2.2 mg of nitrogen per gram of wood. However, ACA treatment only increased the lignin nitrogen content of the wood by 0.24 mg of nitrogen per gram (Table 5.10). Therefore, either only a small proportion of the extra nitrogen added to wood during ACA treatment becomes bound to lignin, or, alternatively, some lignin-bound nitrogen, most probably that fixed by cation exchange mechanisms, was removed by the periodate treatment.

During soil burial, untreated blocks showed a continuous accumulation of nitrogen on the lignin fraction (Table 5.10, Fig 5.6) which was also associated with a continued increase in the total nitrogen content of the

blocks, as a result of microbial invasion of the wood, and with continued decay throughout the burial period. The percentage of total nitrogen on the lignin fraction of the untreated blocks also increased during soil burial (Fig 5.7) showing that nitrogen accumulated more rapidly in lignin than in other wood constituents and confirming the findings of Kane (*op cit*). This accumulation of nitrogen on lignin during the decomposition of wood may be attributed to nitrogen released from wood constituents during decay but more especially nitrogen in forms such as ammonium ions, amino acids and proteins released during autolysis of dead micro-organisms and subsequently becoming attached to lignin.

Such nitrogenous compounds attached to lignin in an exchangeable form would be released into solution in response to a fall in the concentration of soluble nitrogen in the wood and could maintain nitrogen availability to wood decaying micro-organisms. However, nitrogenous compounds complexed with or covalently bound to the lignin would only be released when the lignin itself was being degraded and although the lignin in untreated pine blocks was apparently being depleted as early as the first 6 weeks of soil burial (Table 5.7), lignin is not thought to be heavily attacked during the early stages of soft-rot decay of wood. Therefore, nitrogen permanently bound to lignin is only likely to be mineralised and available to soft-rot microfungi late in the decay process. Such mineralisation

of lignin-bound nitrogen during lignin decomposition could account for the fall in the lignin nitrogen content of lime blocks at high weight loss values observed by Kane (*op cit*). However, the untreated pine blocks used in the present experiment only reached about 22% weight loss by the end of the burial period and this level of decay was clearly not sufficient to cause mineralisation of lignin-bound nitrogen.

The lignin nitrogen content of ACA treated pine blocks remained constant during the first 6 weeks of soil burial (Table 5.10, Fig 5.6). Over the same period, the total nitrogen content of the blocks fell (Table 5.6, Fig 5.4) as a result of loss of soluble nitrogenous compounds from the ACA treated wood to the soil. Consequently, the percentage of the total wood nitrogen bound to lignin was higher in blocks sampled after 6 weeks of soil burial than in unburied control blocks (Table 5.11, Fig 5.7). Therefore, the nitrogen in the form of ammonium and cupr-ammonium ions, which becomes attached to lignin during ACA treatment, appears to be totally resistant to leaching from wood in soil, suggesting the presence of strong complexes or covalent bonds between this added nitrogen and the lignin. The observed loss of nitrogen from ACA treated wood blocks during the first six weeks of soil burial must therefore be from sources not associated with lignin, probably unfixed ammonium salts and ammonia complexed with precipitated preservative deposits.

Accumulation of nitrogen on the lignin fraction of ACA treated blocks during soil burial only started beyond the 6 week sampling interval (Table 5.10, Fig 5.6), coinciding with an increase in the total nitrogen content of the wood (Table 5.6, Fig 5.4). Beyond the 12 week sampling interval, the rate of accumulation of nitrogen on lignin increased (Fig 5.6), corresponding with the onset of decay (Fig 5.3). Thus, as was the case for untreated pine blocks, nitrogen accumulation on the lignin fraction of ACA treated pine blocks was apparently associated with both microbial invasion, as determined by increases in total wood nitrogen content, and decay. In ACA treated wood, accumulation of microbial and wood nitrogen on lignin during decay may be supplemented by solubilisation of some of the extra nitrogen fixed or precipitated in the wood as a result of ACA treatment.

As nitrogen accumulated on the lignin fraction of the ACA treated blocks, the percentage of total wood nitrogen bound to the lignin also increased (Fig 5.11) in a similar manner to that observed in untreated blocks. By the end of the burial period, ACA treated blocks contained a higher percentage of lignin-bound nitrogen than untreated blocks (nearly 50% as compared to less than 42% for the untreated blocks) despite the fact that the accumulation of nitrogen in the whole wood during the decay process was considerably greater in the untreated blocks (the total nitrogen content

of untreated blocks increased from 0.080% $\frac{w}{w}$ to 0.376% $\frac{w}{w}$ whilst that of ACA treated blocks increased from a minimum of 0.201% $\frac{w}{w}$ to just 0.274% $\frac{w}{w}$). Therefore, a larger proportion of the nitrogen entering the wood from the soil accumulated on the lignin in ACA treated wood than in untreated wood. A possible explanation of this observation is that the presence of toxic preservative elements in the ACA treated wood caused the death and subsequent lysis of much of the microbial biomass entering the wood, leading to the release of microbial nitrogen which could then become bound to lignin. In untreated wood, where no toxic elements were present, the proportion of dead microbial biomass should be far lower and consequently less microbial nitrogen should be released into the wood and become bound to lignin.

Comparison of untreated and ACA treated unburied control blocks for mg of lignin copper per g of wood (Table 5.14) shows that the ACA treated blocks only contained about twice as much lignin-bound copper as the untreated blocks, despite the fact that the % $\frac{w}{w}$ copper content of whole ACA treated blocks was more than ten times that of untreated blocks (Table 5.12). The percentage of total wood copper isolated with the lignin fraction of ACA treated blocks only amounted to 4.44% (Table 5.15) whilst the percentage lignin content of the wood was about 27% (Table 5.7). This suggests that, in ACA treated wood, copper may not be bound to lignin in

significant quantities. However, since copper, in the form of cuprammonium ions is thought to become bound to cation exchange sites on wood (Hulme, 1979), it is unlikely that as little as 4.44% of the total copper in ACA treated wood would be bound to lignin. It is therefore more likely that the periodate treatment of the ACA treated wood removed copper fixed to lignin by cation exchange mechanisms: the pH of the periodate solution was 4.1 and may have been sufficiently low to facilitate almost complete removal of cation exchange fixed copper from the lignin.

The quantity of lignin-bound copper in ACA treated wood remained constant during soil burial (Table 5.14) and the percentage of total copper bound to lignin only increased from 4.44% to 6.29% by the end of the burial period (Table 5.15). Since the quantity of lignin-bound copper in the ACA treated blocks was so small, any changes in lignin copper content during soil burial can be considered negligible.

This experiment has confirmed the finding of Kane (*op cit*) and King, Mowe, Bruce and Smith (*op cit*) that nitrogen accumulates on the lignin fraction of wood during decomposition in soil. The significance of such lignin-bound nitrogen in the decay process cannot easily be evaluated, but since nitrogen is the major limiting nutrient to soft-rot microfungi decaying wood, any release of

exchangeable nitrogen or mineralisation of nitrogen bound more permanently to lignin could provide considerable support to the decay process. Lignin-bound nitrogen could play a more important role in the decay of preservative treated wood, since, in the present experiment, a much larger proportion of the total nitrogen entering wood from the soil became bound to lignin in ACA treated blocks than in untreated blocks. Maintainance of nitrogen availability in preservative treated wood by exchangeable lignin-bound nitrogen could not only support the decay process but also help to overcome the toxicity of the preservative.

This experiment has also shown that lignin may play some part in the fixation of ammonia in ACA treated wood: aqueous ammonia may undergo condensation reactions with functional groups on lignin and hence become covalently bound to the lignin. It is also likely that a considerable number of ammonium and cuprammonium ions become fixed to cation exchange sites on lignin during the treatment of wood with ACA. However, such exchangeable ions would appear to have been removed from the lignin during the periodate treatment procedure. Such removal of exchangeable ions from lignin probably also accounts for the very small quantities of copper isolated with lignin from ACA treated wood, since copper would most probably be fixed to lignin mostly as cuprammonium ions by cation exchange mechanisms.

5.4.2 Leaching studies on CCA treated periodate lignin, holocellulose and normal wood

In terms of the aims of this experiment, the following main conclusions can be drawn:

1. Selective absorption ratios for all three preservative elements generally exceeded one in CCA treated normal, delignified and periodate blocks of both lime and pine (Table 5.17). The ratio for each wood type was invariably highest for arsenic and lowest for copper. Ratios for chromium and arsenic were lowest in delignified wood but highest in periodate lignin for lime and normal wood for pine.

2. During aqueous leaching, blocks of all wood types showed some losses of all three preservative elements. For both lime and pine, percentage losses of copper were greatest in delignified blocks and lowest in normal blocks (Table 5.18). Percentage losses of chromium were also greatest from delignified blocks but losses from normal and periodate blocks of lime and pine were minimal. Percentage losses of arsenic were similar from normal and delignified blocks of lime and pine but much lower from periodate blocks.

3. The atom ratios of chromium and arsenic relative to copper were higher in CCA treated normal, delignified and periodate blocks of lime and pine than in the CCA treating

solution (Table 5.19). The ratios of chromium and arsenic relative to copper were generally higher in normal and periodate blocks than in delignified blocks. During aqueous leaching of CCA treated blocks of all wood types, there was a further increase in the ratios of chromium and arsenic relative to copper (Table 5.19). For arsenic, this increase was relatively small, but leached delignified and periodate blocks of lime and pine showed large increases in the ratio of chromium to copper.

Chemical analysis of unleached blocks for % $\frac{W}{W}$ copper, chromium and arsenic contents showed that concentrations of all three elements were highest in delignified blocks and lowest in periodate lignin blocks for both lime and pine (Table 5.16). The delignified blocks of both wood species took up marginally more CCA solution than normal blocks during impregnation. Although the external volume of the blocks remained unchanged during delignification, the removal of lignin must have left more available space inside the blocks for uptake of preservative solution. However, the main factor responsible for the higher % $\frac{W}{W}$ preservative concentrations in delignified blocks was the lower mass of these blocks when compared to the normal blocks, leading to a higher ratio of preservative elements to wood substance in the CCA treated delignified blocks.

The periodate lignin blocks were much smaller than the normal and delignified blocks and had lower % $\frac{w}{w}$ concentrations of preservative elements since they took up less preservative solution during impregnation in relation to the weight of wood substance. It is possible that during impregnation of wood with preservative solution, the polysaccharide components absorb the solution, acting like a sponge, whereas lignin, which is more hydrophobic, does not absorb aqueous solution so readily.

Comparison of preservative concentrations in blocks before and after aqueous leaching (Table 5.16) shows that, in most cases, the concentrations of copper, chromium and arsenic were, as expected, lower in leached blocks. In normal and delignified lime blocks, the chromium concentrations were slightly higher in leached blocks. However, the differences between the chromium concentrations in these blocks and the corresponding unleached controls were not statistically significant and simply reflect the very low percentage loss of chromium from these blocks during aqueous leaching.

The selective absorption ratios of copper, chromium and arsenic in unleached controls of all wood types (Table 5.17) generally exceeded one, showing that blocks took up more of each preservative element during impregnation than would be predicted from uptake of preservative solution.

Such selective absorption of preservative elements, previously observed in normal wood by Smith and Williams (1973b), Henshaw (1979) and King, Smith, Baecker and Bruce (1981), probably results primarily from adsorption, cation exchange and complexing reactions between preservative elements and the wood constituents during impregnation, leading to a fall in the concentration of preservative elements in solution in the wood spaces and a consequent diffusion of further elements into the wood from the preservative solution outside. The selective absorption ratio was invariably highest for arsenic (Table 5.17), despite it being anionic. This suggests that, during impregnation, arsenic either rapidly forms precipitates with copper and chromium or becomes complexed to wood constituents in combination with cationic metals. The selective absorption ratio was lowest for copper in all wood types (Table 5.17), thus suggesting that during the initial reactions between CCA and wood constituents, chromium, as chromium (III) ions, reacts preferentially with arsenic, as proposed by Smith and Williams (1973b).

The fact that copper, chromium and arsenic were generally selectively absorbed by all wood types (Table 5.17) suggests that the three preservative elements undergo adsorption and fixation reactions with both holocellulose and lignin during impregnation. The selective absorption ratios of both chromium and arsenic were lowest in delignified blocks of lime and pine, suggesting that the

initial reactions of these elements with wood are mostly with the lignin fraction. However, the selective absorption ratio for copper was similar in all wood types, suggesting that both holocellulose and lignin play a similar role in the adsorption, cation exchange fixation and complexing of this element in wood during impregnation.

The percentage losses of copper, chromium and arsenic from blocks of all wood types during aqueous leaching (Table 5.18) show that all blocks lost at least a small proportion of each preservative element. These losses may represent the removal of soluble unreacted salts. However, preservative elements fixed to cation exchange sites on the wood would also be expected to be lost gradually during aqueous leaching.

Despite these preservative losses, the majority of each preservative element was resistant to leaching from blocks of all wood types (Table 5.18). Therefore, all three preservative elements can clearly form insoluble products with both lignin and holocellulose during fixation of CCA to wood. Such insoluble preservative elements would most probably be fixed to the functional groups on lignin, cellulose or hemicellulose by cation exchange or complexing mechanisms or deposited as precipitates in the wood.

Precipitates of CCA such as copper (II) and chromium (III) arsenates and copper (II) chromate would form in all blocks

regardless of the composition of the wood. Therefore, differences in the leachability of preservative elements between different wood types probably reflect differences in the ability of these elements to become bound to lignin and holocellulose by complexing and cation exchange mechanisms. The percentage losses of copper, chromium and arsenic during aqueous leaching were higher from delignified blocks than from periodate lignin blocks for both lime and pine (Table 5.18). This suggests that lignin provides more sites suitable for fixation of the three preservative elements than does holocellulose, which includes both cellulose and hemicellulose.

Of the three preservative elements, chromium was generally most resistant to aqueous leaching and negligible quantities of this element were lost from normal and periodate lignin blocks of both lime and pine (Table 5.18). Chromium is generally highly resistant to leaching from wood treated with type C formulations of CCA, as used in this experiment (Henry and Jeroski, 1967; Wallace, 1968). The very low percentage loss of this element from periodate lignin blocks probably reflects the formation of strong complexes between chromium and lignin, either in the form of the chromium (III) cation or the chromium (VI) anion, possibly forming "chromate bridges" (Pizzi, 1982 a,b,c). However, chromium was also fairly resistant to leaching from delignified blocks (less than 10% was lost) showing that this element also formed

insoluble products in holocellulose, probably in the form of complexes or precipitates involving chromium (III) cations (Dahlgren and Hartford, 1972 a;b;c).

Percentage losses of copper were larger than those of chromium from all wood types (Table 5.18) but a larger percentage of copper was lost from delignified blocks than from normal and periodate blocks. This suggests that lignin provides more suitable sites for cation exchange or complexing of copper (II) ions than does holocellulose. However, since 70 per cent or more of the copper was retained by CCA treated delignified blocks after aqueous leaching, this element clearly formed insoluble products in holocellulose, either in the form of precipitates of copper (II) arsenates (Dahlgren and Hartford, *op cit*) or by complexing or cation exchange fixation of copper (II) ions to functional groups on cellulose or hemicellulose.

Percentage losses of arsenic were calculated using the analytical data from leached blocks and unleached controls and percentage losses of this element are therefore less reliable than those calculated for copper and chromium. However, percentage losses of arsenic were generally lower than those of copper, regardless of wood type. Percentage losses of arsenic were lowest from periodate lignin blocks (Table 5.18), suggesting that the arsenate anion also forms stable complexes with lignin, probably in the form of chromium (III) or copper (II) arsenates complexed to functional groups on lignin. Percentage losses of arsenic

were highest from delignified blocks (Table 5.18), suggesting that holocellulose does not provide as many sites for complexing of arsenic as does lignin. Copper (II) and chromium (III) arsenates may form some complexes with functional groups of cellulose and hemicellulose but these insoluble compounds might instead be precipitated around the polysaccharides in the wood cell walls.

The atom ratios of preservative elements in unleached CCA treated blocks (Table 5.19) show that the ratios of both chromium and arsenic were higher, relative to copper, in treated blocks of all wood types than in the CCA treating solution. These increased ratios reflect the fact that chromium and arsenic were selectively absorbed to a greater degree than copper during the treatment of all wood types with CCA (Table 5.17) and again suggest that chromium reacts preferentially with arsenic during the initial absorption reactions of impregnation, probably forming chromium (III) arsenate. If chromium (III) arsenate is formed in preference to copper (II) arsenates in wood during CCA treatment, fixation of copper most probably results primarily from fixation of copper (II) ions to functional groups on lignin, cellulose and hemicellulose by cation exchange or complexing reactions.

The atom ratios of chromium and arsenic relative to copper were lowest in delignified blocks of lime and pine and higher in normal and periodate blocks (Table 5.19).

Thus, the presence of lignin clearly increased absorption of chromium and arsenic relative to copper, possibly as a result of complexing of chromium (III) arsenate and chromium (VI) anions on lignin.

Comparison of the atom ratios of preservative elements in leached and unleached CCA treated blocks (Table 5.19) shows that, for all wood types, the ratios of both chromium and arsenic, relative to copper, were generally higher in leached blocks than in unleached controls. These increased atom ratios during leaching confirm the fact that, in most cases, a higher percentage of copper was lost during leaching of blocks than of chromium and arsenic (Table 5.18). Thus, chromium and arsenic were more resistant than copper to aqueous leaching from CCA treated normal wood, holocellulose and lignin, adding further weight to the suggestion of Smith and Williams (1973b) that chromium reacts preferentially with arsenic during fixation of CCA to wood. Since the ratios of chromium and arsenic both increased relative to copper, in all wood types, the reactions between chromium and arsenic during fixation must be similar in lignin and holocellulose.

From the results of this experiment, it is not possible to predict fixation reactions for preservative elements with lignin and holocellulose since selective

absorption and leaching data cannot be used to predict the proportion of preservative bound to wood by complexing or cation exchange mechanisms as opposed to preservative simply precipitated within the wood. In addition, since the hemicellulose and lignin may be chemically linked in normal wood cells, forming a matrix encrusting the cellulose microfibrils (Kirk, 1972), the reactions of CCA with pure holocellulose and with pure lignin may not be representative of the reactions of CCA with these components in normal wood.

Both periodate lignin and holocellulose become partially oxidised during their preparation. Lignins become oxidised, to some degree, during periodate treatment, with free phenolic hydroxyl groups being converted first to o-quinones and then to muconic acid (Lai and Sarkanan, 1971). During treatment with hypochlorite, polysaccharides may also be partially oxidised, with the introduction of carboxyl groups (Sjostrom, 1981). Thus, both the lignin and holocellulose preparations used in this experiment were modified and probably contained more sites suitable for complexing and cation exchange fixation of preservative elements than lignin, cellulose and hemicellulose in wood. Therefore, fixation of preservative elements to these wood products may have been greater than would occur to the native compounds in wood in service.

Whilst it is impossible to quantify the extent to which the above modifications changed the fixation of preservative elements to wood constituents, the reactions between CCA and periodate lignin and between CCA and holocellulose may bear some resemblance to those that would occur to the same constituents in whole, unmodified wood. Therefore, even taking account of the oxidative modifications to the periodate lignin and holocellulose, the results of this experiment appear to be in accordance with the view of Pizzi (1982) that lignin plays an important role in the fixation of CCA to wood, since all three preservative elements were more resistant to aqueous leaching from CCA treated periodate lignin than from CCA treated holocellulose. This observation would appear to confirm the formation of leach-resistant complexes between all three preservative elements and lignin and also confirms that lignin provides more suitable sites for complexing of preservatives than holocellulose.

It is also clear that all three preservative elements form insoluble products in holocellulose, although it is unclear whether these products are complexed to the cellulose or hemicellulose or simply precipitated in the blocks. Therefore, since holocellulose comprises more than 70% of the total dry mass of the

wood, most of the CCA in treated wood may be present in the cellulose and hemicellulose, even if lignin contains more sites for cation exchange fixation and complexing of preservative elements.

The relative importance of CCA associated with lignin and CCA associated with the polysaccharides in protecting the wood against soft-rot attack has not yet been established but the importance of each would be expected to change across the wood cell in accordance with the proportions of lignin and polysaccharide present. In the lignin-rich S_3 layer, CCA associated with lignin may be very important in preventing penetration of micro-organisms into the S_2 layer, whilst in the polysaccharide-rich S_2 layer, CCA associated with cellulose and hemicellulose is undoubtedly important in preventing the formation of soft-rot cavities, since only preservative elements present at the site of attack can be toxic to decaying micro-organisms, being absorbed by fungal hyphae (Levi, 1969).

Concluding summary

The two experiments described in this chapter have confirmed that lignin does play a role in the fixation of both nitrogen and preservative elements of CCA and ACA to wood and also binds nitrogen during the decay process in soil.

The studies on lignin nitrogen and copper in untreated and ACA treated pine during soil burial showed that:

1. The lignin fraction of untreated pine contained about 35% of the total wood nitrogen prior to soil burial. The lignin fraction of ACA treated blocks contained more nitrogen than that of untreated blocks, prior to soil burial, but this nitrogen only represented about 20% of the total wood nitrogen and much ammonium nitrogen, possibly fixed to lignin in ACA treated wood by cation exchange mechanisms, may have been removed by the periodate treatment.

2. In both untreated and ACA treated pine blocks, nitrogen accumulated on the lignin fraction during soil burial as part of the decay process; the increase in lignin nitrogen content was associated with both an increase in the total nitrogen content of blocks and with decay.

3. This accumulation of nitrogen on lignin during decay was such that the percentage of total nitrogen bound to

lignin increased during soil burial for both untreated and ACA treated blocks. A larger proportion of the total nitrogen accumulating in the wood became bound to lignin in the ACA treated blocks.

4. Very little copper (amounting to less than 5% of the total wood copper) was isolated with the lignin fraction of ACA treated blocks, suggesting that the periodate treatment removed most of the lignin-bound copper.

The leaching studies on CCA treated periodate lignin, holocellulose and normal wood showed that:

1. Copper, chromium and arsenic were all selectively absorbed by normal wood, holocellulose and periodate lignin during treatment with CCA solution.

2. Although CCA treated normal wood, holocellulose and periodate lignin blocks all showed some losses of copper, chromium and arsenic during aqueous leaching, the majority of each preservative element was resistant to leaching, confirming the formation of insoluble fixation products of CCA in both lignin and holocellulose. However, all three preservative elements were more resistant to leaching from CCA treated periodate lignin blocks than from CCA treated holocellulose blocks.

3. Atom ratios of chromium and arsenic relative to copper were higher in CCA treated normal, holocellulose and

periodate lignin blocks than in the CCA treating solution, showing preferential absorption of chromium and arsenic relative to copper during impregnation. Aqueous leaching of these blocks led to a further increase in the atom ratios of chromium and arsenic relative to copper, showing that chromium and arsenic were more resistant to aqueous leaching from CCA treated blocks of all wood types than was copper.

CHAPTER 6

GENERAL CONCLUSIONS

The studies described in this thesis have given insight into some factors which may affect the performance of CCA and ACA treated wood in soil contact. The factors considered have been: the effects of redistributed soluble nutrients or high nitrogen content in preservative treated wood on its susceptibility to decay; soil factors affecting the leachability of preservative elements from treated wood; fixation processes in CCA and ACA treated wood and factors affecting these processes; the role of lignin in the fixation of both nitrogen and preservative elements to wood.

The CCA soil burial experiment (Chapter 2) clearly showed that soluble nutrients present at wood surfaces increase the susceptibility of CCA treated hardwoods and softwoods to decay when in soil contact. These nutrients, if present in CCA treated service material, could significantly reduce the service life of the timber. Such a problem would be particularly severe in hardwoods with a high nutrient content but might also contribute to the premature failure of CCA treated softwoods, especially in such high risk situations as horticultural soils, which possess a highly active soil microflora and hence render the wood more susceptible to decay than it would be in uncultivated soil.

The CCA soil burial experiment also examined the stability of preservative elements in CCA treated wood in soil. Although percentage losses of toxic elements of

up to 50% were observed at low CCA treating concentrations, at higher preservative loadings, more representative of retentions used in service material, losses of toxic elements were very low. Such small losses should give no cause for concern if repeated in CCA treated timber in service. Further studies at this laboratory (Green, *pers comm*) have confirmed that losses of preservative elements from 3 and 5% $\frac{w}{v}$ CCA treated lime, pine and spruce blocks in soil contact are minimal.

In the CCA soil burial experiment, surface nutrients increased losses of preservative elements from CCA treated wood, although these increased losses were not generally statistically significant. Some of the preservative may have complexed to the soluble, leachable nutrients rather than the wood, possibly partially accounting for the high decay susceptibility of CCA treated wood containing soluble nutrients. Such complexing of preservative elements to soluble nutrients is analogous to a recent hypothesis of Pizzi and Conradie (1986). These authors proposed that, during the impregnation of wood with CCA, preservative elements complex with tannins in the wood in preference to the wood substance. Since certain hardwoods contain high concentrations of tannin, in these woods, insufficient CCA might become fixed to the wood for decay to be prevented. However, none of the wood species used in the present studies are reported to have high tannin contents and it is therefore unlikely that tannins could have contributed

significantly to the failure of CCA treated wood in the CCA soil burial experiment.

Leaching studies using CCA treated wood (Chapter 3) confirmed that neither soluble components of soil nor bacteria in suspension in an aqueous soil extract cause significantly greater losses of preservative elements from CCA treated wood than does distilled water. Aqueous extracts from soils with a low pH or a high concentration of cations would be more likely to influence CCA stability. Fungal secretions might also cause solubilisation of preservative elements (Levi, 1976), but since such fungal solubilisation of CCA would require fungal presence within the wood, significant solubilisation could only occur in wood already subject to microbial invasion.

Aqueous leaching studies on CCA treated wood blocks (Chapter 3) also showed that air-drying of the blocks, after impregnation with preservative and two weeks of wet curing, did not affect the leachability of preservative elements in distilled water. Thus, if a high moisture content is maintained in CCA treated wood, after impregnation, long enough for primary fixation reactions to be completed, the subsequent drying of the wood should not influence preservative stability.

Analysis of unleached ammonia and ACA treated wood (Chapter 3) confirmed that treatment of wood with either

ammonia solution or an ACA preservative solution increased the nitrogen content of the wood. Much of this extra nitrogen was found to be resistent to aqueous leaching and since not all of the additional nitrogen in ammonia and ACA treated wood could be accounted for by ammonium nitrogen analysis, some ammonia must either have been converted to non-ammoniacal nitrogen or have become covalently bound to the wood. Since both the nitrogen and ammonium nitrogen contents of ACA treated wood increased with increasing preservative treating concentration, some of the ammonium nitrogen added to the wood during ACA treatment must have been associated with copper and arsenic.

The concentration of ammonia in the ACA preservative solution was also found to influence the nitrogen content of the ACA treated wood: the nitrogen content of treated blocks increased with increasing ammonia concentration in the preservative solution. This effect was maintained even after aqueous leaching or oven-drying of the blocks. Thus, if the residual extra nitrogen in ACA treated wood can act as a nutrient source to micro-organisms, it might be advantageous to use the minimum amount of ammonia in the ACA treating solution required to keep the copper in solution during the impregnation process. However, minimising the ammonia concentration of the ACA solution would also reduce the penetration of the preservative into refractory wood species.

Aqueous leaching of ACA treated wood blocks (Chapter 3) removed about 20% of the copper from the blocks, regardless of preservative treating concentration. Thus, the copper is not so resistant to aqueous leaching from ACA treated wood as it is from CCA treated wood.

Although the analysis of ACA treated wood blocks showed some association between ammonium nitrogen, total nitrogen and copper concentrations in both leached and unleached samples, no firm conclusions could be drawn regarding the fixation mechanisms of ACA in wood.

A large-scale soil burial experiment using ACA treated wood (Chapter 4) was undertaken to compare the toxic thresholds of copper in ACA treated wood blocks with those in CCA treated wood blocks (Chapter 2). This experiment showed that, at any given equivalent copper concentration, ACA treated wood was more susceptible to decay in soil than CCA treated wood. This higher decay susceptibility of ACA treated wood may have been due, in part, to the high nitrogen content of the wood. However, other factors may also have adversely affected the performance of the ACA treated wood: ACA contains less arsenic than CCA at any given copper concentration and comparison of the performance ACA treated wood with that of CCA treated wood based on copper content alone takes no account of any antimicrobial effects of arsenic; ACA also contains no chromium which might also have some antimicrobial effects in CCA treated

wood; the copper in ACA treated wood is thought to be largely in the form of precipitates (Hulme, 1979) and may therefore be in a form less toxic to micro-organisms than in CCA treated wood.

Losses of copper from unleached ACA treated wood blocks during soil burial generally greatly exceeded the 20% losses observed during aqueous leaching. Such large copper losses must have reduced the toxicity of the wood and may partially account for the poor performance of ACA treated wood in soil in the present studies.

The concentrations of ACA employed in the ACA soil burial programme were far lower than those normally employed in service material and it is therefore difficult to relate the findings of the programme to ACA treated timber in service. Furthermore, ACA is not currently employed in decay susceptible hardwoods in tropical field situations where high concentrations of CCA have already been proven ineffective (McNamara, Greaves and Triana, 1983). The very poor performance of ACA, when compared to CCA, in the present soil burial studies, suggests that ACA would be unlikely to be any more effective than CCA in tropical field situations, even at high concentrations.

Studies on the lignin nitrogen content of untreated and ACA treated wood blocks during soil burial (Chapter 5) confirmed that nitrogen accumulates on lignin during the

early part of the decay process. Although the form of the nitrogen isolated on lignin was not determined, it is unlikely to include many exchangeable ammonium ions since these would most probably have been removed from the lignin during the periodate lignin isolation procedure. Therefore, the observed increase in lignin nitrogen content during the decay process probably resulted from chemical binding of nitrogen to lignin. Such covalently bound nitrogen could only be available as a nitrogen source to wood-decaying micro-organisms once decay is well established and lignin is being broken down. Thus the role of lignin nitrogen in the initiation of the decay process would appear to be minimal.

Copper was not isolated from the periodate lignin fraction of ACA treated wood in significant quantities, probably as a result of removal of any lignin-bound copper by the acidic (pH 4.1) periodate isolation procedure. It is therefore impossible to draw conclusions on the mode of fixation of copper in ACA treated wood from the present studies.

Aqueous leaching of 3% $\frac{w}{v}$ CCA treated normal wood, holocellulose and periodate lignin blocks (Chapter 5) showed that copper, chromium and arsenic undergo reactions in both holocellulose and lignin, forming insoluble products. This suggests that preservative elements are associated with both the polysaccharide and lignin

components in CCA treated wood and both lignin and polysaccharide-bound CCA may be important in preventing decay. However, all three preservative elements were more resistant to aqueous leaching from CCA treated periodate lignin blocks than from CCA treated holocellulose blocks, suggesting that lignin does have a greater capacity to bind copper, chromium and arsenic than the polysaccharides.

The failure of CCA and ACA treated wood in soil

Wood emplaced in soil causes a chemostimulatory response in the soil microflora which initiates a microbial invasion of the wood and a consequent increase in the wood's nitrogen content. It is clear, from the CCA and ACA soil burial experiments (Chapter 2 and 4 respectively), that the presence of these preservatives does not prevent microbial invasion of the wood or nitrogen accumulation. Even if the preservatives prevent immediate soft-rot attack, the presence of fungi in the wood should in time, cause solubilisation of preservative elements (Levi, 1976) and their depletion from the wood substance, either being absorbed by fungal hyphae (Levi, 1969) or leached from the wood. Therefore, unless microbial invasion of the preservative treated wood can be prevented, it seems inevitable that preservative elements will be depleted and threshold levels of microbial inoculum or

nitrogen will be reached above which soft-rot attack can commence.

King, Smith, Baecker and Bruce (1981) observed no nitrogen accumulation in wood blocks treated with high concentrations of CCA. It is therefore possible that high concentrations of heavy metal preservatives in wood may prevent microbial invasion of wood, probably by sterilising the surrounding soil (Smith, 1980). However, such protection of the wood could only continue for a finite period since some preservative would be required to be in solution in the soil, leading to depletion of preservative elements from the wood and a gradual fall in the wood's toxicity to micro-organisms. The aqueous leaching studies on CCA treated wood (Chapter 3) showed continued losses of copper and chromium, at a low level, after six days of leaching, suggesting that preservative elements are indeed gradually depleted from CCA treated wood in the liquid phase. A similar depletion of copper and arsenic would also be expected from ACA treated wood in soil contact.

For wood treated with a high concentration of either CCA or ACA, the time required for the preservative concentration in the wood to fall to a level where decay can commence should depend on the preservative treating concentration. Smith (1980) observed an increase in the "induction phase" prior to decay with increasing CCA

treating concentration and attributed this to loss of preservative elements from the wood, with samples containing higher concentrations of CCA requiring a longer period of preservative depletion prior to the onset of decay.

In some tropical environments, very high loadings of CCA do not prevent the rapid onset of decay in eucalypt (Leightley and Norton, 1981; McNamara, Greaves and Triana, 1983), probably as a result of either rapid leaching of preservative elements or a highly active soil microflora. However, in some temperate or dry environments, preservative depletion from CCA or ACA treated wood may take many years, giving the wood an acceptable service life. In addition, in temperate regions, most timber used in soil contact situations is of the softwood type which generally performs well when treated with CCA or ACA. However, despite the excellent service record of CCA treated softwoods in temperate regions, the service life of such material is finite and unless some means can be found to prevent microbial invasion of wood in soil, the eventual failure of all timber treated with heavy metal preservatives and emplaced in soil seems inevitable.

In conclusion, the main findings of the present studies have been that:

1. Concentrations of soluble nutrients at wood surfaces increase the toxic thresholds of CCA in both the hardwood lime and the softwood pine.

2. The leachability of preservative elements from CCA treated wood, in the aqueous phase, is not increased by the presence in solution of soil extractives or by the presence of bacteria in suspension.

3. In soil burial studies, the toxic thresholds of copper are higher in ACA treated wood than in CCA treated wood.

4. Nitrogen accumulates on the lignin fraction of both untreated and ACA treated pine wood blocks during the early stages of the decay process.

5. All three preservative elements of CCA react with both the lignin and polysaccharide components of wood to form insoluble products, although all elements were more resistant to aquous leaching from CCA treated periodate lignin than from CCA treated holocellulose.

Future studies

Following the studies described in this thesis, further experimentation in several areas would be useful as a continuation of the work undertaken.

It is not, at present, clear whether concentrations of soluble nutrients are present at the surface of large pieces of CCA treated service material, Therefore, nitrogen analyses should be undertaken on CCA treated timber to determine whether or not a nitrogen-rich surface profile exists after preservative treatment. If surface nutrients do exist in service material, aqueous leaching of timber prior to preservative treatment might improve the service life of the wood. Further studies could be undertaken to determine the effect of such pre-leaching on the final performance of CCA treated wood in service.

There is currently little reliable information on the stability of preservative elements in CCA treated wood in service since timber is not chemically analysed prior to emplacement in soil. Studies should be undertaken using large pieces of CCA treated timber to determine whether or not preservative elements are lost from such material in soil contact. Analysis of samples after various periods of emplacement in soil would give an indication of whether preservative elements are lost from the timber and, if so, over what time scale. Nitrogen analyses on these samples prior to and during decay would also show whether or not microbial invasion (as measured by an increase in nitrogen content), observed in small CCA treated blocks in the laboratory, also occurs at the surface of service material.

Since the wood blocks used in the ACA soil burial experiment (Chapter 4) were only treated with very low concentrations of the preservative, a further, longer term soil burial experiment should be undertaken using blocks of both hardwoods and softwoods treated with much higher concentrations of ACA. Samples treated with high concentrations of CCA should be included for comparison of decay susceptibility. Total nitrogen, ammonium nitrogen, copper and arsenic analysis of the ACA treated wood should show whether or not the high nitrogen content of the wood affects the performance in a similar way to that observed in wood blocks treated with lower concentrations of ACA.

The experiment isolating periodate lignin and studying the lignin nitrogen content of untreated and ACA treated pine blocks during soil burial (Chapter 5) should be repeated using both lime and pine blocks with more preservative treating concentrations. The use of the decay-susceptible lime and a longer burial period, allowing heavy decay of pine blocks should allow the fate of lignin-bound nitrogen during the latter part of the decay process to be determined.

Although copper could not be isolated on the lignin fraction of ACA treated wood using the periodate procedure, it is possible that differences in the fixation mechanism of CCA to wood might allow preservative elements to be

isolated on the periodate lignin fraction of CCA treated wood. Thus, an experiment could be undertaken to isolate periodate lignin from CCA treated lime and pine blocks. Analysis of the periodate blocks and normal CCA treated blocks might further elucidate the role of lignin in the binding of CCA to wood.

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APPENDIX I

MEAN % WEIGHT LOSS, % MOISTURE CONTENT, ANALYTICAL % $\frac{W}{W}$ NITROGEN, COPPER, CHROMIUM AND ARSENIC CONCENTRATION AND THEORETICAL PRESERVATIVE CONCENTRATIONS (CALCULATED FROM UPTAKE OF PRESERVATIVE SOLUTION) FOR UNTREATED AND CCA TREATED PINE, BEECH AND LIME BLOCKS DURING SOIL BURIAL.

TABLE 1 MEAN % WEIGHT LOSSES (±STANDARD DEVIATIONS) FOR UNTREATED AND CCA TREATED PINE, BEECH AND LIME BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type	$\%^{w}_{v}$ CCA	Sampling Period (Weeks)				
		3	6	9	12	18
Pine Centre	0	-	4.0 ± 0.9	-	12.0 ± 3.0	19.6 ± 1.6
	0.25	-	0.9 ± 0.4	-	2.5 ± 2.2	8.1 ± 3.1
	0.50	-	1.0 ± 0.7	-	0.7 ± 0.4	2.9 ± 1.9
	0.75	-	0.8 ± 0.5	-	0 ± 0.1	1.1 ± 0.4
	1.00	-	0.9 ± 0.6	-	0 ± 0	1.5 ± 0.5
	1.50	-	0.7 ± 0.7	-	0 ± 0.1	1.0 ± 0.7
Pine RSN	0	-	9.9 ± 2.6	-	20.6 ± 2.5	23.3 ± 1.5
	0.25	-	7.0 ± 2.5	-	16.5 ± 3.1	22.2 ± 6.6
	0.50	-	6.6 ± 1.7	-	13.4 ± 4.6	11.2 ± 3.4
	0.75	-	5.7 ± 0.8	-	10.5 ± 2.5	10.5 ± 3.4
	1.00	-	5.9 ± 1.8	-	6.3 ± 1.7	8.7 ± 1.8
	1.50	-	5.1 ± 1.6	-	5.0 ± 1.1	6.2 ± 1.9
Beech	0	9.1 ± 0.9	32.1 ± 13.2	40.2 ± 9.5	41.4 ± 15.6	47.8 ± 18.1
	0.5	4.7 ± 2.0	17.0 ± 12.2	26.0 ± 14.3	35.7 ± 8.2	37.0 ± 17.4
	1.0	2.7 ± 0.7	6.5 ± 2.0	17.7 ± 8.5	18.4 ± 5.1	30.2 ± 7.2
	1.5	1.2 ± 0.5	3.3 ± 0.7	7.7 ± 2.6	12.9 ± 3.1	31.0 ± 1.7
	2.0	1.2 ± 0.3	3.9 ± 1.5	7.8 ± 3.9	19.9 ± 8.5	23.2 ± 3.1
	2.5	0.6 ± 0.4	2.3 ± 1.3	4.4 ± 2.3	11.9 ± 4.1	12.1 ± 5.4
	3.0	0.4 ± 0.3	1.9 ± 1.2	5.8 ± 3.5	11.5 ± 3.7	14.5 ± 8.0
Lime Centre	0	9.2 ± 3.5	30.0 ± 12.5	56.8 ± 19.1	48.5 ± 7.2	57.9 ± 8.2
	0.5	1.7 ± 0.5	5.6 ± 1.4	12.8 ± 3.5	16.9 ± 5.9	34.1 ± 8.8
	1.0	0.6 ± 0.3	1.9 ± 0.9	4.7 ± 1.8	4.3 ± 1.2	11.5 ± 4.6
	1.5	0.2 ± 0.2	1.0 ± 0.7	2.3 ± 1.3	2.2 ± 0.7	7.6 ± 3.4
	2.0	0 ± 0.8	0.6 ± 0.7	2.6 ± 0.6	0.8 ± 0.9	4.4 ± 1.7
Lime RSN	0	20.3 ± 4.4	40.5 ± 10.7	53.7 ± 16.6	59.3 ± 25.5	60.9 ± 9.3
	0.5	13.5 ± 2.9	28.1 ± 6.9	42.6 ± 9.9	47.8 ± 8.9	53.1 ± 7.5
	1.0	14.6 ± 4.3	19.7 ± 8.6	29.0 ± 6.6	32.0 ± 6.0	43.1 ± 6.9
	1.5	9.8 ± 2.7	14.3 ± 6.4	15.5 ± 5.7	20.3 ± 6.0	32.2 ± 3.1
	2.0	10.7 ± 2.8	13.9 ± 5.9	14.7 ± 4.2	32.5 ± 9.3	32.4 ± 10.8
	2.5	10.0 ± 4.6	10.4 ± 2.3	14.3 ± 4.0	25.6 ± 10.2	37.1 ± 7.6
	3.0	10.6 ± 5.3	9.9 ± 2.8	12.1 ± 4.8	14.3 ± 5.7	28.8 ± 8.0

TABLE 2 MEAN % MOISTURE CONTENT (± STANDARD DEVIATION) FOR UNTREATED AND CCA TREATED PINE, BEECH AND LIME BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE POST-BURIAL DRY MASS.

Wood Type	$\%^{w}_{v}$ CCA	Sampling Period (Weeks)				
		3	6	9	12	18
Pine Centre	0	-	165.4± 10.2	-	200.0± 6.8	242.2± 75.5
	0.25	-	157.0± 12.4	-	165.0± 11.5	195.5± 23.1
	0.50	-	142.6± 15.8	-	146.7± 8.4	168.0± 17.7
	0.75	-	111.0± 19.2	-	107.5± 17.2	114.3± 15.4
	1.00	-	114.7± 25.9	-	102.4± 14.5	108.8± 12.6
	1.50	-	93.5± 7.1	-	94.5± 7.0	101.1± 6.8
Pine RSN	0	-	173.9± 9.2	-	199.2± 6.4	253.4± 26.7
	0.25	-	171.9± 15.5	-	186.8± 19.0	237.2± 14.4
	0.50	-	173.3± 17.3	-	186.2± 15.2	191.5± 22.6
	0.75	-	168.0± 12.7	-	170.2± 8.5	174.0± 10.3
	1.00	-	156.9± 8.3	-	164.8± 9.4	163.9± 11.8
	1.50	-	146.6± 15.9	-	158.2± 20.9	161.4± 16.6
Beech	0	72.5±10.9	109.0± 31.0	175.3± 38.5	219.0±104.1	240.2± 75/3
	0.5	57.7± 9.7	101.0± 45.3	129.8± 36.2	199.5± 20.2	213.6± 62.8
	1.0	52.9± 5.7	70.6± 27.1	121.0± 39.0	117.7± 33.4	168.5± 35.4
	1.5	49.3± 4.1	58.6± 6.2	95.3± 11.7	119.0±105.9	140.5± 42.1
	2.0	48.3±10.5	52.1± 5.4	97.0± 17.2	144.6± 33.7	157.8± 51.9
	2.5	48.0± 4.9	50.0± 2.2	71.7± 9.4	116.7± 26.5	128.4± 31.7
	3.0	51.4± 1.0	50.7± 5.6	75.2± 6.8	118.7± 47.2	131.7± 26.3
Lime Centre	0	121.9±56.1	155.1±121.6	265.4± 71.5	336.1± 83.6	357.8±103.4
	0.5	60.7±11.7	78.8± 16.2	133.5± 22.4	199.4± 71.8	267.1± 78.5
	1.0	56.6± 6.7	56.4± 16.7	62.6± 11.6	79.8± 19.3	129.7± 24.7
	1.5	53.8± 7.5	53.2± 9.9	58.4± 6.6	71.9± 17.2	102.3± 11.9
	2.0	64.9±11.9	49.0± 8.5	59.9± 12.8	63.1± 9.4	70.8± 6.1
Lime RSN	0	121.3±28.7	215.5±143.1	303.7±121.2	342.8±114.4	339.5±108.7
	0.5	85.2±23.3	151.1± 47.4	197.6± 81.8	228.5± 92.3	270.6± 75.7
	1.0	105.4±33.9	117.6± 83.7	158.2± 31.3	161.1± 48.7	188.2± 61.0
	1.5	84.1±12.1	104.4± 25.0	129.3± 11.5	137.3± 23.8	165.4± 42.9
	2.0	107.6±31.9	109.1± 37.0	118.6± 33.5	141.7± 19.0	158.5± 27.1
	2.5	92.0±26.6	66.3± 35.1	78.9± 14.9	101.4± 10.4	137.3± 33.1
	3.0	98.8±17.9	110.4± 26.0	99.9± 24.8	126.2± 17.6	134.0± 16.8

TABLE 3 MEAN $\%^{w}_{w}$ NITROGEN CONCENTRATION (± STANDARD DEVIATIONS) FOR UNTREATED CCA-TREATED PINE, BEECH AND LIME BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type	$\%^{w}_{v}$ CCA	Sampling Period (Weeks)					
		0	3	6	9	12	18
Pine Centre	0	0.061 (±0.012)	-	0.196 (±0.030)	-	0.338 (±0.055)	0.298 (±0.067)
	0.25	0.070 (±0.014)	-	0.150 (±0.011)	-	0.243 (±0.025)	0.229 (±0.027)
	0.50	0.073 (±0.011)	-	0.174 (±0.032)	-	0.242 (±0.017)	0.208 (±0.019)
	0.75	0.079 (±0.017)	-	0.189 (±0.018)	-	0.200 (±0.024)	0.181 (±0.009)
	1.00	0.096 (±0.009)	-	0.230 (±0.022)	-	0.207 (±0.018)	0.183 (±0.009)
	1.50	0.096 (±0.011)	-	0.186 (±0.025)	-	0.200 (±0.009)	0.189 (±0.016)
	Av	0.079					
Pine RSN	0	0. 151 (±0. 018)	-	0.220 (±0.022)	-	0.272 (±0.021)	0.338 (±0.019)
	0.25	0. 151 (±0. 025)	-	0.167 (±0.011)	-	0.302 (±0.060)	0.365 (±0.062)
	0.50	0. 171 (±0. 030)	-	0.181 (±0.029)	-	0.280 (±0.040)	0.301 (±0.056)
	0.75	0. 183 (±0. 025)	-	0.186 (±0.017)	-	0.276 (±0.039)	0.248 (±0.024)
	1.00	0. 174 (±0. 024)	-	0.221 (±0.016)	-	0.285 (±0.039)	0.221 (±0.017)
	1.50	0. 153 (±0. 031)	-	0.212 (±0.025)	-	0.307 (±0.042)	0.240 (±0.031)
	Av	0.164					
Beech	0	0.096 (±0.024)	0.184 (±0.022)	0.302 (±0.030)	0.384 (±0.074)	0.341 (±0.031)	0.249 (±0.041)
	0.5	0.114 (±0.021)	0.177 (±0.047)	0.227 (±0.020)	0.344 (±0.063)	0.405 (±0.047)	0.361 (±0.071)
	1.0	0.124 (±0.025)	0.156 (±0.025)	0.204 (±0.070)	0.349 (±0.024)	0.346 (±0.051)	0.274 (±0.025)
	1.5	0.136 (±0.032)	0.150 (±0.038)	0.210 (±0.024)	0.211 (±0.049)	0.331 (±0.059)	0.373 (±0.086)
	2.0	0.131 (±0.025)	0.112 (±0.010)	0.174 (±0.034)	0.256 (±0.047)	0.300 (±0.067)	0.201 (±0.075)
	2.5	0.122 (±0.022)	0.129 (±0.018)	0.218 (±0.053)	0.217 (±0.072)	0.277 (±0.089)	0.276 (±0.047)
	3.0	0.108 (±0.009)	0.135 (±0.017)	0.168 (±0.043)	0.243 (±0.035)	0.257 (±0.023)	0.295 (±0.058)

TABLE 3 (CONTINUED)

Wood Type	%w/w CCA	Sampling Period (Weeks)					
		0	3	6	9	12	18
Lime Centre	0	0.144 (±0.007)	0.273 (±0.056)	0.413 (±0.045)	0.449 (±0.012)	0.457 (±0.079)	0.433 (±0.097)
	0.5	0.152 (±0.017)	0.179 (±0.022)	0.308 (±0.035)	0.361 (±0.046)	0.372 (±0.031)	0.444 (±0.129)
	1.0	0.127 (±0.023)	0.175 (±0.013)	0.208 (±0.028)	0.240 (±0.036)	0.246 (±0.030)	0.331 (±0.102)
	1.5	0.150 (±0.014)	0.152 (±0.018)	0.207 (±0.022)	0.199 (±0.025)	0.202 (±0.032)	0.215 (±0.023)
	2.0	0.132 (±0.014)	0.144 (±0.013)	0.231 (±0.012)	0.164 (±0.031)	0.197 (±0.014)	0.235 (±0.027)
	Av	0.135					
Lime RSN	0	0.197 (±0.018)	0.290 (±0.031)	0.459 (±0.084)	0.397 (±0.062)	0.406 (±0.079)	0.465 (±0.098)
	0.5	0.235 (±0.030)	0.250 (±0.047)	0.425 (±0.067)	0.460 (±0.147)	0.529 (±0.053)	0.594 (±0.017)
	1.0	0.223 (±0.028)	0.305 (±0.100)	0.363 (±0.039)	0.439 (±0.033)	0.448 (±0.086)	0.555 (±0.084)
	1.5	0.191 (±0.038)	0.226 (±0.010)	0.290 (±0.024)	0.342 (±0.128)	0.418 (±0.045)	0.576 (±0.059)
	2.0	0.210 (±0.024)	0.271 (±0.026)	0.305 (±0.027)	0.318 (±0.044)	0.467 (±0.060)	0.502 (±0.067)
	2.5	0.210 (±0.026)	0.230 (±0.019)	0.344 (±0.041)	0.269 (±0.035)	0.405 (±0.040)	0.573 (±0.024)
	3.0	0.216 (±0.051)	0.274 (±0.038)	0.299 (±0.033)	0.315 (±0.063)	0.346 (±0.072)	0.537 (±0.085)
	Av	0.212					

TABLE 4 MEAN % $\frac{w}{w}$ COPPER CONCENTRATION (± STANDARD DEVIATION) FOR UNTREATED AND CCA TREATED PINE, BEECH AND LIME BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type		Sampling Period (Weeks)					
		0	3	6	9	12	18
Pine Centre	0			0.009 (±0.001)		0.011 (±0.003)	0.016 (±0.004)
	0.25	0.034 (±0.009)		0.024 (±0.002)		0.027 (±0.002)	027 (±0.001)
	0.50	0.062 (±0.005)		0.046 (±0.002)		0.045 (±0.003)	044 (±0.003)
	0.75	0.090 (±0.014)		0.063 (±0.008)		0.069 (±0.004)	064 (±0.005)
	1.00	0.127 (±0.015)		0.092 (±0.009)		0.094 (±0.004)	094 (±0.010)
	1.50	0.175 (±0.012)		0.122 (±0.012)		0.147 (±0.005)	150 (±0.004)
Pine RSN	0			0.004 (±0.002)		0.005 (±0.001)	0.012 (±0.001)
	0.25	0.030 (±0.001)		0.018 (±0.001)		0.015 (±0.004)	018 (±0.002)
	0.50	0.058 (±0.002)		0.032 (±0.003)		0.031 (±0.005)	036 (±0.002)
	0.75	0.086 (±0.010)		0.063 (±0.015)		0.045 (±0.006)	054 (±0.006)
	1.00	0.113 (±0.012)		0.085 (±0.010)		0.072 (±0.005)	069 (±0.005)
	1.50	0.167 (±0.010)		0.120 (±0.022)		0.117 (±0.021)	110 (±0.012)
Beech	0		0.018 (±0.002)	0.011 (±0.002)	0.014 (±0.011)	0.004 (±0.001)	0.007 (±0.002)
	0.5	0.039 (±0.006)	0.041 (±0.005)	0.030 (±0.004)	0.020 (±0.003)	0.020 (±0.003)	0.024 (±0.004)
	1.0	0.078 (±0.002)	0.039 (±0.011)	0.060 (±0.011)	0.048 (±0 004	0.053 (±0.006)	0.046 (±0.006)
	1.5	0.108 (±0.014)	0.054 (±0.005)	0.099 (±0.008)	0.096 (±0.013)	0.099 (±0.011)	0.086 (±0.005)
	2.0	0.133 (±0.021)	0.102 (±0.022)	0.099 (±0.005)	0.096 (±0.020)	0.102 (±0.021)	0.090 (±0.017)
	2.5	0.142 (±0.039)	0.128 (±0.019)	0.134 (±0.022)	0.136 (±0.018)	0.123 (±0.022)	0.133 (±0.021)
	3.0	0.143 (±0.019	0.163 (±0.037)	0.173 (±0.021)	0.138 (±0.019)	0.149 (±0.026)	0.147 (±0.022)

TABLE 4 (CONTINUED)

Wood Type	%$^{W}_{V}$ CCA	Sampling Interval (Weeks)					
		0	3	6	9	12	18
Lime Centre	0		0.011 (±0.007)	0.008 (±0.002)	0.006 (±0.007)	0.009 (±0.004)	0.007 (±0.007)
	0.5	0.071 (±0.026)	0.069 (±0.071)	0.063 (±0.009)	0.058 (±0.008)	0.061 (±0.005)	0.053 (±0.010)
	1.0	0.142 (±0.014)	0.152 (±0.018)	0.114 (±0.013)	0.122 (±0.013)	0.131 (±0.010)	0.121 (±0.017)
	1.5	0.257 (±0.065)	0.183 (±0.019)	0.171 (±0.021)	0.183 (±0.016)	0.170 (±0.011)	0.182 (±0.016)
	2.0	0.173 (±0.040)	0.170 (±0.027)	0.211 (±0.040)	0.189 (±0.031)	0.192 (±0.023)	0.180 (±0.030)
Lime RSN	0		0.003 (±0.002)	0.009 (±0.002)	0.009 (±0.004)	0.013 (±0.002)	0.010 (±0.003)
	0.5	0.059 (±0.007)	0.040 (±0.015)	0.035 (±0.009)	0.033 (±0.004)	0.044 (±0.006)	0.036 (±0.004)
	1.0		0.071 (±0.009)	0.083 (±0.013)	0.083 (±0.010)	0.094 (±0.010)	0.069 (±0.003)
	1.5	0.201 (±0.031)	0.134 (±0.020)	0.147 (±0.017)	0.154 (±0.027)	0.151 (±0.023)	0.112 (±0.019)
	2.0	0.210 (±0.011)	0.148 (±0.036)	0.150 (±0.013)	0.151 (±0.028)	0.146 (±0.019)	0.120 (±0.012)
	2.5	0.257 (±0.026)	0.179 (±0.046)	0.201 (±0.007)	0.189 (±0.044)	0.188 (±0.017)	0.163 (±0.020)
	3.0	0.266 (±0.025)	0.197 (±0.025)	0.242 (±0.037)	0.231 (±0.038)	0.256 (±0.053)	0.204 (±0.018)

TABLE 5 MEAN $\%^{W}_{w}$ CHROMIUM CONCENTRATIONS (± STANDARD DEVIATION) FOR UNTREATED AND CCA TREATED PINE, BEECH AND LIME BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type	$\%^{W}_{w}$ CCA	Sampling Period (Weeks)					
		0	3	6	9	12	18
Pine Centre	0		-	0.004	-	0.011	0.015
			-	(±0.005)	-	(±0.011)	(±0.021)
	0.25	0.035	-	0.050	-	0.053	0.052
		(±0.009)	-	(±0.008)	-	(±0.005)	(±0.001)
	0.50	0.085	-	0.108	-	0.111	0.106
		(±0.010)	-	(±0.013)	-	(±0.010)	(±0.002)
	0.75	0.192	-	0.150	-	0.171	0.152
		(±0.042)	-	(±0.015)	-	(±0.014)	(±0.005)
	1.00	0.254	-	0.200	-	0.232	0.190
		(±0.050)	-	(±0.020)	-	(±0.007)	(±0.006)
	1.50	0.399	-	0.319	-	0.384	0.366
		(±0.024)	-	(±0.037)	-	(±0.034)	(±0.013)
Pine RSN	0		-	0.010	-	0.007	0.014
			-	(±0.008)	-	(±0.005)	(±0.008)
	0.25	0.054	-	0.030	-	0.026	0.025
		(±0.004)	-	(±0.008)	-	(±0.007)	(±0.010)
	0.50	0.119	-	0.063	-	0.057	0.070
		(±0.007)	-	(±0.009)	-	(±0.003)	(±0.015)
	0.75	0.183	-	0.118	-	0.099	0.122
		(±0.039)	-	(±0.027)	-	(±0.014)	(±0.030)
	1.00	0.269	-	0.182	-	0.178	0.149
		(±0.044)	-	(±0.022)	-	(±0.020)	(±0.010)
	1.50	0.347	-	0.310	-	0.313	0.260
		(±0.074)	-	(±0.024)	-	(±0.026)	(±0.033)
Beech	0		0.005	0.005	0.027	0.008	0.009
			(±0.002)	(±0.004)	(±0.026)	(±0.009)	(±0.060)
	0.5	0.085	0.059	0.048	0.052	0.039	0.052
		(±0.010)	(±0.007)	(±0.005)	(±0.004)	(±0.006)	(±0.007)
	1.0	0.157	0.060	0.125	0.116	0.128	0.102
		(±0.029)	(±0.014)	(±0.014)	(±0.020)	(±0.011)	(±0.015)
	1.5	0.274	0.118	0.267	0.247	0.249	0.268
		(±0.033)	(±0.026)	(±0.022)	(±0.035)	(±0.032)	(±0.015)
	2.0	0.261	0.206	0.230	0.195	0.226	0.207
		(±0.021)	(±0.045)	(±0.014)	(±0.030)	(±0.041)	(±0.027)
	2.5	0.353	0.293	0.317	0.281	0.307	0.308
		(±0.064)	(±0.057)	(±0.037)	(±0.040)	(±0.040)	(±0.038)
	3.0	0.354	0.333	0.349	0.300	0.317	0.322
		(±0.024)	(±0.063)	(±0.063)	(±0.042)	(±0.060)	(±0.042)

TABLE 5 (CONTINUED)

Wood Type	%$^{w}_{v}$ CCA	Sampling Period (Weeks)					
		0	3	6	9	12	18
Lime Centre	0		0.011 (±0.003)	0.003 (±0.012)	0.012 (±0.009)	0.005 (±0.001)	0.009 (±0.003)
	0.5	0.119 (±0.039)	0.107 (±0.045)	0.117 (±0.023)	0.116 (±0.021)	0.128 (±0.013)	0.113 (±0.016)
	1.0	0.232 (±0.016)	0.315 (±0.023)	0.227 (±0.014)	0.233 (±0.048)	0.281 (±0.028)	0.244 (±0.037)
	1.5	0.488 (±0.106)	0.326 (±0.101)	0.397 (±0.050)	0.390 (±0.047)	0.403 (±0.021)	0.427 (±0.051)
	2.0	0.381 (±0.047)	0.326 (±0.079)	0.448 (±0.088)	0.373 (±0.104)	0.426 (±0.049)	0.436 (±0.083)
Lime RSN	0		0.007 (±0.009)	0.005 (±0.010)	0.013 (±0.008)	0.013 (±0.016)	0.016 (±0.014)
	0.5	0.117 (±0.012)	0.066 (±0.016)	0.071 (±0.025)	0.080 (±0.019)	0.079 (±0.012)	0.072 (±0.012)
	1.0		0.135 (±0.054)	0.189 (±0.035)	0.197 (±0.027)	0.203 (±0.008)	0. (±0.)
	1.5	0.422 (±0.051)	0.342 (±0.033)	0.338 (±0.101)	0.342 (±0.092)	0.387 (±0.028)	0.282 (±0.023)
	2.0	0.406 (±0.044)	0.280 (±0.065)	0.318 (±0.030)	0.292 (±0.040)	0.266 (±0.046)	0.276 (±0.032)
	2.5	0.508 (±0.087)	0.326 (±0.160)	0.450 (±0.041)	0.440 (±0.142)	0.399 (±0.087)	0.412 (±0.039)
	3.0	0.503 (±0.052)	0.465 (±0.067)	0.529 (±0.047)	0.529 (±0.070)	0.534 (±0.089)	0.476 (±0.050)

TABLE 6 MEAN $\%^{w}_{w}$ ARSENIC CONCENTRATION (± STANDARD DEVIATION) FOR UNTREATED AND CCA TREATED PINE, BEECH AND LIME BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type	$\%^{w}_{w}$ CCA	Sampling Period (Weeks)					
		0	3	6	9	12	18
Pine Centre	0			0		0.016	0.012
				0		(±0.017)	(±0.022)
	0.25	0.079		0.052		0.046	0.040
		(±0.011)		(±0.039)		(±0.030)	(±0.018)
	0.50	0.119		0.110		0.085	0.109
		(±0.062)		(±0.038)		(±0.005)	(±0.036)
	0.75	0.179		0.136		0.107	0.113
		(±0.086)		(±0.045)		(±0.023)	(±0.022)
	1.00	0.180		0.193		0.143	0.164
		(±0.037)		(±0.041)		(±0.031)	(±0.048)
	1.50	0.215		0.273		0.245	0.306
		(±0.037)		(±0.020)		(±0.025)	(±0.016)
Pine RSN	0			0.014		0.007	0.011
				(±0.022)		(±0.005)	(±0.013)
	0.25	0.087		0.041		0.017	0.039
		(±0.050)		(±0.042)		(±0.017)	(±0.012)
	0.50	0.125		0.106		0.032	0.051
		(±0.018)		(±0.031)		(±0.026)	(±0.009)
	0.75	0.178		0.115		0.078	0.068
		(±0.034)		(±0.023)		(±0.027)	(±0.017)
	1.00	0.199		0.134		0.079	0.133
		(±0.037)		(±0.047)		(±0.024)	(±0.048)
	1.50	0.284		0.158		0.217	0.241
		(±0.058)		(±0.029)		(±0.091)	(±0.046)
Beech	0		0.008	0	0.021	0.002	0.002
			(±0.007)	0	(±0.021)	(±0.005)	(±0.004)
	0.5	0.103	0.022	0.039	0.019	0.022	0.015
		(±0.035)	(±0.012)	(±0.013)	(±0.007)	(±0.007)	(±0.009)
	1.0	0.238	0.046	0.092	0.051	0.074	0.059
		(±0.085)	(±0.024)	(±0.047)	(±0.018)	(±0.028)	(±0.009)
	1.5	0.244	0.101	0.133	0.139	0.143	0.142
		(±0.038)	(±0.023)	(±0.031)	(±0.064)	(±0.029)	(±0.016)
	2.0	0.269	0.226	0.139	0.130	0.153	0.103
		(±0.066)	(±0.049)	(±0.054)	(±0.061)	(±0.025)	(±0.019)
	2.5	0.325	0.341	0.177	0.218	0.185	0.219
		(±0.129)	(±0.068)	(±0.036)	(±0.058)	(±0.041)	(±0.038)
	3.0	0.343	0.347	0.223	0.251	0.215	0.262
		(±0.082)	(±0.090)	(±0.031)	(±0.035)	(±0.037)	(±0.042)

TABLE 6 (CONTINUED)

Wood Type	%W/W CCA	Sampling Period (Weeks)					
		0	3	6	9	12	18
Lime Centre	0		0.041 (±0.040)			0.020 (±0.007)	0.039 (±0.024)
	0.5	0.141 (±0.050)	0.162 (±0.049)	0.140 (±0.080)	0.095 (±0.019)	0.075 (±0.009)	0.092 (±0.033)
	1.0	0.198 (±0.034)	0.200 (±0.018)	0.196 (±0.081)	0.273 (±0.041)	0.212 (±0.034)	0.158 (±0.048)
	1.5	0.372 (±0.054)	0.273 (±0.065)	0.309 (±0.048)	0.275 (±0.092)	0.288 (±0.023)	0.301 (±0.055)
	2.0	0.418 (±0.065)	0.218 (±0.103)	0.325 (±0.062)	0.303 (±0.061)	0.310 (±0.045)	0.274 (±0.032)
Lime RSN	0		0.014 (±0.014)	0 (± 0)	(± 0)	0.015 (±0.017)	0.011 (±0)
	0.5	0.087 (±0.034)	0.007 (±0.015)	0.081 (±0.039)	0.077 (±0.015)	0.061 (±0.007)	0.069 (±0.080)
	1.0		0.122 (±0.202)	0.121 (±0.063)	0.130 (±0.070)	0.136 (±0.020)	0.122 (±0.052)
	1.5	0.387 (±0.106)	0.185 (±0.096)	0.283 (±0.088)	0.321 (±0.065)	0.247 (±0.037)	0.164 (±0.016)
	2.0	0.275 (±0.100)	0.416 (±0.199)	0.277 (±0.032)	0.265 (±0.095)	0.303 (±0.079)	0.252 (±0.071)
	2.5	0.419 (±0.261)	0.557 (±0.165)	0.412 (±0.063)	0.312 (±0.094)	0.234 (±0.042)	0.357 (±0.105)
	3.0	0.638 (±0.177)	0.726 (±0.334)	0.531 (±0.154)	0.378 (±0.100)	0.435 (±0.133)	0.365 (±0.115)

TABLE 7 THEORETICAL $\%^{w}_{w}$ COPPER, CHROMIUM AND ARSENIC CONCENTRATIONS IN UNBURIED CCA TREATED PINE, BEECH AND LIME BLOCKS, CALCULATED FROM UPTAKE OF PRESERVATIVE SOLUTION.

Wood Type	$\%^{w}_{v}$ CCA	Theoretical $\%^{w}_{w}$ Concentration		
		Copper	Chromium	Arsenic
Pine Centre	0.25	0.025	0.045	0.031
	0.50	0.056	0.101	0.070
	0.75	0.065	0.118	0 081
	1.00	0.105	0 185	0.131
	1.50	0.147	0.278	0 183
Pine RSN	0.25	0 022	0 039	0 027
	0.50	0 056	0.100	0 070
	0.75	0.077	0.137	0 096
	1.00	0.106	0.189	0.132
	1.50	0.158	0.282	0.197
Beech	0.5	0.030	0.053	0.037
	1.0	0.070	0.125	0.087
	1.5	0.113	0.202	0.141
	2.0	0.128	0.228	0.159
	2.5	0.169	0.302	0.211
	3.0	0.194	0.346	0.242
Lime Centre	0.5	0.058	0.103	0.072
	1.0	0.117	0.209	0.146
	1.5	0.218	0.389	0.272
	2.0	0.194	0.346	0.242
Lime RSN	0.5	0.043	0.077	0.054
	1.0	0.101	0.180	0.126
	1.5	0.190	0.339	0.237
	2.0	0.203	0.362	0.253
	2.5	0.271	0.484	0.338
	3.0	0.315	0.562	0.392

APPENDIX 2

MEAN % WEIGHT LOSS, % MOISTURE CONTENT AND ANALYTICAL % $\frac{W}{W}$ TOTAL NITROGEN, AMMONIUM NITROGEN, NON-AMMONIACAL NITROGEN AND COPPER CONCENTRATION IN UNTREATED, AMMONIA TREATED AND ACA TREATED LIME, PINE AND SPRUCE BLOCKS DURING SOIL BURIAL.

TABLE 1 % WEIGHT LOSS (± STANDARD DEVIATION) OF UNTREATED, AMMONIA TREATED AND ACA TREATED LIME, PINE AND SPRUCE BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type	Treating Solution	Percentage Weight Loss Sampling Interval (Weeks)		
		6	12	18
Unleached Lime	Untreated	20.0±3.0	30.2±4.1	37.9±6.1
	1.35%$\overset{W}{v}$NH$_3$	23.1±3.5	36.5±3.1	43.2±2.9
	0.028%$\overset{W}{v}$ACA	22.0±2.8	36.0±8.1	43.0±4.6
	0.071%$\overset{W}{v}$ACA	15.8±2.9	26.5±2.4	36.3±4.1
	0.142%$\overset{W}{v}$ACA	9.6±2.1	21.6±1.4	28.0±6.1
	0.283%$\overset{W}{v}$ACA	7.7±2.2	13.7±3.3	19.5±4.8
Leached Lime	Untreated	18.7±2.7	30.1±2.1	38.7±4.8
	1.35%$\overset{W}{v}$NH$_3$	23.2±2.3	33.3±3.1	41.9±7.4
	0.028%$\overset{W}{v}$ACA	22.8±3.4	33.7±3.2	40.2±5.1
	0.071%$\overset{W}{v}$ACA	19.3±2.4	25.0±3.3	33.0±4.3
	0.142%$\overset{W}{v}$ACA	12.7±4.3	20.9±2.6	25.9±2.8
	0.283%$\overset{W}{v}$ACA	4.4±2.4	10.6±4.2	13.5±4.6
Pine	Untreated	3.5±1.1	13.5±1.3	22.1±1.3
	1.35%$\overset{W}{v}$NH$_3$	4.0±0.7	11.7±2.8	23.5±1.8
	0.028%$\overset{W}{v}$ACA	1.6±1.4	10.5±1.6	23.0±2.7
	0.071%$\overset{W}{v}$ACA	0.4±0.7	6.7±2.6	19.7±1.6
	0.142%$\overset{W}{v}$ACA	+1.0±1.0	0.8±0.6	4.8±3.9
	0.283%$\overset{W}{v}$ACA	+0.6±0.7	0.4±4.6	1.1±0.8
Spruce	Untreated	1.9±1.7	14.2±2.3	21.6±1.2
	1.35%$\overset{W}{v}$NH$_3$	2.7±1.6	14.4±0.7	20.4±1.9
	0.028%$\overset{W}{v}$ACA	0.1±0.9	6.3±1.9	15.2±3.3
	0.071%$\overset{W}{v}$ACA	+2.0±1.5	2.7±3.6	6.8±5.1
	0.142%$\overset{W}{v}$ACA	+3.7±2.9	0.1±2.4	+0.7±1.9
	0.283%$\overset{W}{v}$ACA	+2.6±1.1	+1.3±2.2	+2.8±1.4

TABLE 2 % MOISTURE CONTENTS (± STANDARD DEVIATIONS) OF UNTREATED, AMMONIA TREATED AND ACA TREATED LIME, PINE AND SPRUCE BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE POST-BURIAL DRY MASS.

Wood Type	Treating Solution	Sampling Interval (Weeks)		
		6	12	18
Unleached Lime	0	206.5±22.6	213.4±25.1	227.2±15.2
	NH_3	212.1±19.9	219.8±16.7	219.7±26.9
	0.057	214.0±19.7	235.6±14.9	227.1±13.5
	0.142	201.2± 7.8	218.2±24.9	234.2±42.3
	0.283	190.3± 7.3	219.7±17.7	224.6±25.0
	0.566	169.7±13.8	193.2±12.6	192.4±21.3
Leached Lime	0	195.7±20.4	227.5±11.7	252.1±25.5
	NH_3	218.4± 9.6	239.7±33.0	257.6±50.6
	0.057	210.3±22.3	255.1±25.4	252.4±19.5
	0.142	212.9±16.2	215.3±51.6	233.9±20.4
	0.283	185.6±12.2	199.4±37.8	227.7± 7.1
	0.566	126.4±14.9	171.3±23.2	156.5±38.8
Pine	0	171.9± 9.4	194.3±10.7	206.0±14.2
	NH_3	175.4± 9.6	202.9±11.7	197.8± 7.8
	0.023	176.6±13.9	183.8± 3.9	204.7±10.3
	0.057	160.4± 9.6	179.3±14.7	189.1±16.9
	0.142	171.1±15.7	168.9±12.7	165.5±11.3
	0.283	170.6±12.9	157.3± 6.7	157.2±14.1
Spruce	0	219.0±28.9	251.5±34.6	272.2±22.6
	NH_3	245.5±13.8	260.1±36.7	264.9±23.1
	0.023	190.3±13.4	223.7±27.0	222.4±13.7
	0.057	207.6±20.6	216.3±22.1	194.7±15.0
	0.142	186.0±18.5	188.2±18.3	182.0±15.1
	0.283	189.5±25.9	183.8±20.4	184.0±34.3

TABLE 3 $\%^{w}_{w}$ NITROGEN CONCENTRATION (± STANDARD DEVIATION) OF UNTREATED AMMONIA TREATED AND ACA TREATED LIME, PINE AND SPRUCE BLOCKS DURING SOIL BURIAL, EXPRESSED AS A PERCENTAGE OF THE PRE-BURIAL DRY MASS.

Wood Type	Treating Solution	Sampling Interval (Weeks)			
		0	6	12	18
Unleached Lime	Untreated	0.155±0.032	0.312±0.033	0.349±0.040	0.325±0.022
	1.35$\%^{w}_{v}NH_3$	0.358±0.027	0.385±0.028	0.364±0.048	0.346±0.021
	0.028$\%^{w}_{v}$ACA	0.373±0.049	0.369±0.026	0.398±0.033	0.356±0.022
	0.071$\%^{w}_{v}$ACA	0.373±0.060	0.351±0.021	0.470±0.056	0.480±0.034
	0.142$\%^{w}_{v}$ACA	0.413±0.059	0.370±0.017	0.485±0.027	0.551±0.054
	0.283$\%^{w}_{v}$ACA	0.438±0.023	0.358±0.023	0.424±0.037	0.563±0.056
Leached Lime	Untreated	0.138±0.012	0.364±0.039	0.319±0.027	0.428±0.023
	1.35$\%^{w}_{v}NH_3$	0.260±0.010	0.410±0.024	0.373±0.047	0.391±0.061
	0.028$\%^{w}_{v}$ACA	0.247±0.030	0.432±0.032	0.414±0.056	0.441±0.024
	0.071$\%^{w}_{v}$ACA	0.256±0.031	0.493±0.047	0.436±0.036	0.474±0.048
	0.142$\%^{w}_{v}$ACA	0.264±0.040	0.476±0.050	0.458±0.019	0.497±0.057
	0.283$\%^{w}_{v}$ACA	0.304±0.053	0.485±0.037	0.426±0.050	0.446±0.039
Pine	Untreated	0.080±0.005	0.215±0.012	0.340±0.024	0.376±0.007
	1.35$\%^{w}_{v}NH_3$	0.224±0.003	0.289±0.015	0.398±0.019	0.375±0.018
	0.028$\%^{w}_{v}$ACA	0.259±0.023	0.246±0.018	0.386±0.014	0.394±0.031
	0.071$\%^{w}_{v}$ACA	0.283±0.017	0.202±0.019	0.388±0.027	0.397±0.010
	0.142$\%^{w}_{v}$ACA	0.300±0.030	0.201±0.017	0.274±0.016	0.264±0.019
	0.283$\%^{w}_{v}$ACA	0.332±0.017	0.246±0.022	0.231±0.021	0.236±0.010
Spruce	Untreated	0.124±0.008	0.205±0.020	0.293±0.031	0.418±0.028
	1.35$\%^{w}_{v}NH_3$	0.227±0.015	0.257±0.039	0.378±0.037	0.427±0.050
	0.028$\%^{w}_{v}$ACA	0.266±0.012	0.225±0.036	0.326±0.019	0.420±0.052
	0.071$\%^{w}_{v}$ACA	0.315±0.034	0.220±0.018	0.257±0.031	0.358±0.026
	0.142$\%^{w}_{v}$ACA	0.317±0.018	0.209±0.022	0.228±0.015	0.269±0.011
	0.283$\%^{w}_{v}$ACA	0.351±0.021	0.254±0.032	0.251±0.017	0.276±0.020

TABLE 4 $\%^{w}_{w}$ NON-AMMONIACAL NITROGEN CONCENTRATION IN UNTREATED, AMMONIA TREATED AND ACA TREATED LIME, PINE AND SPRUCE BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type	Treating Solution	Sampling Interval (weeks)			
		0	6	12	18
Unleached Lime	Untreated	0.130	0.291	0.328	0.305
	1.35$\%^{w}_{v}NH_3$	0.244	0.363	0.336	0.319
	0.028$\%^{w}_{v}$ACA	0.245	0.335	0.366	0.327
	0.071$\%^{w}_{v}$ACA	0.243	0.329	0.434	0.446
	0.142$\%^{w}_{v}$ACA	0.285	0.336	0.450	0.516
	0.283$\%^{w}_{v}$ACA	0.291	0.322	0.386	0.524
Leached Lime	Untreated	0.128	0.343	0.296	0.405
	1.35$\%^{w}_{v}NH_3$	0.213	0.377	0.342	0.361
	0.028$\%^{w}_{v}$ACA	0.197	0.398	0.378	0.404
	0.071$\%^{w}_{v}$ACA	0.203	0.454	0.396	0.434
	0.142$\%^{w}_{v}$ACA	0.218	0.437	0.412	0.454
	0.283$\%^{w}_{v}$ACA	0.250	0.446	0.382	0.403
Pine	Untreated	0.061	0.196	0.321	0.357
	1.35$\%^{w}_{v}NH_3$	0.128	0.257	0.366	0.345
	0.028$\%^{w}_{v}$ACA	0.156	0.213	0.353	0.361
	0.071$\%^{w}_{v}$ACA	0.173	0.172	0.355	0.364
	0.142$\%^{w}_{v}$ACA	0.187	0.170	0.242	0.231
	0.283$\%^{w}_{v}$ACA	0.221	0.216	0.198	0.202
Spruce	Untreated	0.103	0.186	0.273	0.400
	1.35$\%^{w}_{v}NH_3$	0.135	0.232	0.348	0.397
	0.028$\%^{w}_{v}$ACA	0.171	0.199	0.294	0.391
	0.071$\%^{w}_{v}$ACA	0.198	0.188	0.226	0.326
	0.142$\%^{w}_{v}$ACA	0.202	0.172	0.196	0.237
	0.283$\%^{w}_{v}$ACA	0.224	0.217	0.220	0.244

TABLE 5 $\%^{w}_{w}$ AMMONIUM NITROGEN CONCENTRATION (± STANDARD DEVIATION) OF UNTREATED, AMMONIA TREATED AND ACA TREATED LIME, PINE AND SPRUCE BLOCKS DURING SOIL BURIAL, EXPRESSED AS A % OF THE PRE-BURIAL DRY MASS.

Wood Type	Treating Solution	Sampling Interval (Weeks)			
		0	6	12	18
Unleached Lime	Untreated	0.025±0.003	0.021±0.002	0.021±0.003	0.020±0.002
	1.35$\%^{w}_{v}NH_3$	0.114±0.005	0.022±0.003	0.028±0.003	0.027±0.003
	0.028$\%^{w}_{v}$ACA	0.128±0.001	0.034±0.002	0.032±0.004	0.029±0.003
	0.071$\%^{w}_{v}$ACA	0.130±0.004	0.032±0.003	0.036±0.003	0.036±0.003
	0.142$\%^{w}_{v}$ACA	0.128±0.008	0.034±0.003	0.035±0.005	0.035±0.004
	0.283$\%^{w}_{v}$ACA	0.147±0.018	0.036±0.003	0.038±0.003	0.039±0.003
Leached Lime	Untreated	0.010±0.003	0.021±0.001	0.023±0.002	0.023±0.005
	1.35$\%^{w}_{v}NH_3$	0.047±0.001	0.033±0.002	0.031±0.002	0.030±0.002
	0.028$\%^{w}_{v}$ACA	0.050±0.001	0.034±0.002	0.036±0.003	0.037±0.003
	0.071$\%^{w}_{v}$ACA	0.053±0.004	0.039±0.003	0.040±0.002	0.040±0.002
	0.142$\%^{w}_{v}$ACA	0.046±0.002	0.039±0.002	0.046±0.005	0.043±0.003
	0.283$\%^{w}_{v}$ACA	0.054±0.002	0.039±0.004	0.044±0.003	0.043±0.003
Pine	Untreated	0.019±0.001	0.019±0.002	0.019±0.002	0.019±0.002
	1.35$\%^{w}_{v}NH_3$	0.096±0.008	0.032±0.003	0.032±0.004	0.030±0.002
	0.028$\%^{w}_{v}$ACA	0.103±0.017	0.033±0.009	0.033±0.005	0.033±0.003
	0.071$\%^{w}_{v}$ACA	0.110±0.004	0.030±0.002	0.033±0.002	0.033±0.003
	0.142$\%^{w}_{v}$ACA	0.113±0.04	0.031±0.002	0.032±0.002	0.033±0.003
	0.283$\%^{w}_{v}$ACA	0.111±0.004	0.030±0.001	0.033±0.004	0.034±0.004
Spruce	Untreated	0.021±0.002	0.019±0.002	0.020±0.002	0.018±0.001
	1.35$\%^{w}_{v}NH_3$	0.092±0.020	0.025±0.003	0.030±0.003	0.030±0.003
	0.028$\%^{w}_{v}$ACA	0.095±0.005	0.026±0.002	0.032±0.003	0.029±0.003
	0.071$\%^{w}_{v}$ACA	0.107±0.015	0.032±0.004	0.031±0.002	0.032±0.003
	0.142$\%^{w}_{v}$ACA	0.115±0.040	0.037±0.005	0.032±0.003	0.032±0.003
	0.283$\%^{w}_{v}$ACA	0.127±0.025	0.037±0.002	0.031±0.002	0.032±0.003

TABLE 6 $\%^{w}_{w}$ COPPER CONCENTRATION (± STANDARD DEVIATION) OF UNTREATED, AMMONIA TREATED AND ACA TREATED LIME, PINE AND SPRUCE BLOCKS DURING SOIL BURIAL, EXPRESSED AS A PERCENTAGE OF THE PRE-BURIAL DRY MASS.

Wood Type	Treating Solution	Sampling Interval (Weeks)			
		0	6	12	18
Unleached Lime	Untreated	0.015±0.002	0.011±0.001	0.012±0.003	0.011±0.001
	1.35% $^{w}_{v}$ NH_3	0.015±0.001	0.009±0.002	0.011±0.002	0.011±0.002
	0.028% $^{w}_{v}$ ACA	0.048±0.004	0.032±0.004	0.032±0.004	0.023±0.002
	0.071% $^{w}_{v}$ ACA	0.108±0.014	0.067±0.005	0.074±0.007	0.057±0.008
	0.142% $^{w}_{v}$ ACA	0.161±0.019	0.109±0.017	0.123±0.012	0.124±0.007
	0.283% $^{w}_{v}$ ACA	0.286±0.039	0.136±0.031	0.205±0.008	0.202±0.012
Leached Lime	Untreated	0.015±0.001	0.016±0.002	0.009±0.001	0.015±0.002
	1.35% $^{w}_{v}$ NH_3	0.020±0.001	0.018±0.007	0.013±0.003	0.017±0.004
	0.028% $^{w}_{v}$ ACA	0.051±0.010	0.051±0.008	0.042±0.006	0.043±0.007
	0.071% $^{w}_{v}$ ACA	0.088±0.014	0.084±0.012	0.078±0.005	0.070±0.014
	0.142% $^{w}_{v}$ ACA	0.126±0.014	0.132±0.017	0.123±0.015	0.123±0.013
	0.283% $^{w}_{v}$ ACA	0.245±0.038	0.226±0.026	0.185±0.020	0.199±0.019
Pine	Untreated	0.009±0.002	0.016±0.003	0.014±0.002	0.014±0.001
	1.35% $^{w}_{v}$ NH_3	0.006±0.002	0.012±0.002	0.014±0.002	0.013±0.002
	0.028% $^{w}_{v}$ ACA	0.035±0.009	0.027±0.004	0.024±0.002	0.024±0.003
	0.071% $^{w}_{v}$ ACA	0.050±0.004	0.041±0.002	0.040±0.003	0.038±0.005
	0.142% $^{w}_{v}$ ACA	0.098±0.007	0.075±0.007	0.075±0.003	0.070±0.008
	0.283% $^{w}_{v}$ ACA	0.147±0.013	0.014±0.008	0.097±0.007	0.103±0.009
Spruce	Untreated	0.015±0.001	0.012±0.002	0.009±0.001	0.016±0.003
	1.35% $^{w}_{v}$ NH_3	0.015±0.002	0.012±0.001	0.007±0.001	0.014±0.001
	0.028% $^{w}_{v}$ ACA	0.038±0.006	0.037±0.007	0.027±0.005	0.036±0.004
	0.071% $^{w}_{v}$ ACA	0.069±0.017	0.069±0.013	0.042±0.003	0.060±0.011
	0.142% $^{w}_{v}$ ACA	0.105±0.014	0.111±0.018	0.081±0.005	0.081±0.004
	0.283% $^{w}_{v}$ ACA	0.156±0.011	0.137±0.015	0.112±0.016	0.098±0.008